

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> <b>A61L 15/22, 15/58, 15/60</b> <b>C09J 157/00</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/09633</b> <b>(43) International Publication Date:</b> <b>11 July 1991 (11.07.91)</b>
<b>(21) International Application Number:</b> <b>PCT/US90/07412</b> <b>(22) International Filing Date:</b> <b>13 December 1990 (13.12.90)</b>  <b>(30) Priority data:</b> <b>458,246</b> <b>28 December 1989 (28.12.89)</b> <b>US</b>		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).	
<b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133 (US).		<b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(72) Inventor:</b> ASMUS, Robert, A. ; P.O. Box 33427, Saint Paul, MN 55133 (US).			
<b>(74) Agents:</b> HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133 (US).			

**(54) Title:** COMPOSITE OF A DISPERSED GEL IN AN ADHESIVE MATRIX AND METHOD FOR PREPARING SAME**(57) Abstract**

A composite of a gel of swollen hydrocolloid dispersed in a pressure sensitive adhesive matrix is provided. The gel has a natural or synthetically derived hydrocolloid swollen with a non-volatile swelling agent, such that the gel may have a shear modulus of less than  $6.2 \times 10^6$  dynes/cm<sup>2</sup>. The gel-adhesive composite has continued skin adhesion whether applied to or existing in dry or moist skin conditions. The gel contributes a high moisture vapor transmission rate to attempt to maintain dry skin conditions while the adhesive maintains skin adhesion. The gel-adhesive composite may be used in a variety of tape, dressing, bandage, drape, or other skin contacting usage and may optionally include antimicrobial agents to treat the skin while adhesion continues.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BC	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

-1-

COMPOSITE OF A DISPERSED GEL IN AN ADHESIVE MATRIX  
AND METHOD FOR PREPARING SAME

5

Field Of The Invention

The present invention relates to novel  
composites of gels of swollen hydrocolloids dispersed in  
10 a pressure sensitive adhesive matrix. The present  
invention also relates to the preparation of such  
composites, which are useful in medical applications,  
such as tapes, dressings, drapes, and antimicrobial  
devices.

15

Background Of The Invention

A hydrocolloid is a synthetically prepared or  
naturally occurring polymer capable of forming a  
thickened gel in the presence of water and polyols.

20

Hydrogels, hydrocolloids swollen with water or  
another hydrophilic liquid have been known for the  
purpose of absorbing or retaining moisture or water.  
U.S. Patents 4,438,258 and 4,552,138 describe typical  
hydrogels.

25

In medical applications, hydrogels swollen with  
water or other liquids generally have good moisture vapor  
transmission rates. Hydrogels are quite useful for the  
absorbing or removal of body fluids, such as  
perspiration, from the pores of the continuous skin of  
the patient or from a wound, incision or other opening in  
30 the skin of the patient.

35

While certain hydrogels can have some pressure  
sensitive adhesive properties, the adhesive strength of  
hydrogels is marginal for general utility skin adhesives.  
Hydrogels alone are generally not used as medical tapes,  
dressings, drapes and the like because of lack of good  
adhesive strength in either dry skin environments ("dry

-2-

stick adhesion") or in moist skin environments ("wet stick adhesion"). Both of these environments require continuous strong adhesion of a tape, dressing, bandage or the like for proper patient care.

5 On the other hand, conventional pressure sensitive adhesives have strong dry stick adhesion, but often lack high moisture vapor transmission properties. For this reason, the adhesion may fail in moist environments occurring beneath medical tapes, dressings, 10 drapes and the like.

15 Also, if antimicrobial agents, such as chlorhexidine, are desired to be administered topically to the skin of the patient, these pressure sensitive adhesives alone are poor candidates to provide rapid delivery of the antimicrobial agent to the skin.

20 Conventional pressure sensitive adhesives have been mixed with unswollen hydrocolloidal filler material for the purpose of providing wet stick adhesion where initial moist skin environments are common. For example, U.S. Patents 4,166,051 and 4,505,976 describe adhesives with hydrocolloids mixed therein. These mixtures are used as sealants about a skin opening of a patient, such as a stoma, following surgery.

25 A stoma sealant requires wet stick adhesion to absorb or wick away moisture or other body fluids from about the skin opening. However, the use of unswollen hydrocolloidal fillers or reinforcers initially make the adhesive much stiffer and less pliable, reducing the dry stick adhesion of the adhesive against the flexible contours of the movable and stretchable skin.

30 Furthermore, following the continued absorbance of moisture and other body fluids, inevitably, wet stick adhesion is also reduced. Also such stoma-type adhesives are typically opaque, which, while not important for their usefulness about stomas, limit their usefulness 35

-3-

where transparent or nearly transparent adhesives are desired in medical applications such as for incise drapes.

Thus, the use of hydrocolloids in the medical 5 applications has progressed in diverging directions. In one direction, swollen hydrocolloids. Hydrogels provide high moisture vapor transmission rates but without significant dry or wet stick adhesive strength. In the other direction, unswollen hydrocolloids mixed into conventional pressure sensitive adhesives to become 10 opaque stoma-type sealants provide wet stick adhesion at the expense of dry stick adhesion.

What is needed in the art is a composite which 15 has the good dry stick adhesion of a strong pressure sensitive adhesive and the high moisture vapor transmission rate of a swollen hydrocolloid. It is desirable to have a composite which has the capability of avoiding loss of adhesion against the skin or skin opening upon continued exposure to moist conditions. It 20 is also desirable to have an adhesive which has translucency approaching transparency and has the ability to release antimicrobial agents in efficacious amounts when placed in contact with the skin.

25

#### Summary Of The Invention

30

The present invention provides a composite of a gel dispersed in an adhesive matrix which continuously transmits moisture vapor while continuously adhered to the skin of a patient. The gel-adhesive composite of the present invention is at least nearly transparent, has a high moisture vapor transmission rate, and has a high peel strength.

35

The composite is a two phase system of gel and adhesive, where the dispersed phase of the system is a two component gel.

-4-

The gel-adhesive composite requires at least three components: (1) a pressure sensitive adhesive as the continuous matrix; and in the dispersed gel, (2) a hydrocolloid and (3) a swelling agent for the hydrocolloid.

5           The gel-adhesive composite comprises from about 5 weight percent to about 99 weight percent of a pressure sensitive adhesive composition and from about 1 weight percent to about 95 weight percent of a gel dispersed in the pressure sensitive adhesive composition, the gel comprising a hydrocolloid and a non-volatile hydrocolloid swelling agent having a ratio of weight fractions of hydrocolloid to swelling agent of from about 3:1 to about 1:99.

10           The pressure sensitive adhesive may be a conventional pressure sensitive adhesive, which is defined by the Pressure Sensitive Tape Council (Glossary of Terms Used in Pressure Sensitive Tape Industry, PSTC, Glenview, Ill. 1959) to be adhesives "which in dry form are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure." These adhesives "have a sufficiently cohesive holding and elastic nature so that, despite their aggressive tackiness, they can be handled with the fingers and removed from smooth surfaces without leaving a residue." Because pressure sensitive adhesives vary in their strength of adhesiveness, their selection for use in the composite will depend on the final application desired.

15           The pressure sensitive adhesive is preferably hydrophobic, i.e., tending neither to combine with nor be soluble in water. The natural lack of affinity for water possessed by a hydrophobic pressure sensitive adhesive causes it to separate from and remain immiscible with water or other hydrophilic liquids.

-5-

The swelling agent is a hydrophilic liquid, i.e., tending to combine with and be soluble in water. The natural affinity for water of the swelling agent allows the swelling agent to swell the hydrocolloid, defined above, keeping the swollen hydrocolloid, the gel, separated from and dispersed in the pressure sensitive adhesive.

The difference in hydrophilicity of the swelling agent to the pressure sensitive adhesive sufficient to generate a two phase system, i.e., their incompatibility, is required to maintain sufficient amounts of swelling agent in the hydrocolloidal gel particles dispersed in the pressure sensitive adhesive matrix and to minimize plasticization of the pressure sensitive adhesive, which would cause loss of skin adhesion and increase adhesive residue. Optimally, no amount of swelling agent should migrate into the pressure sensitive adhesive. Preferably, less than 0.5 weight percent of the pressure sensitive adhesive matrix should comprise migrated swelling agent. In no event should more than 5 weight percent of the pressure sensitive matrix comprise migrated swelling agent. In no event should the amount of swelling agent migrated into the pressure adhesive matrix cause the gel to have a ratio of weight fractions of hydrocolloid to swelling agent exceeding about 3:1.

The swelling agent must also be non-volatile, i.e., essentially non-evaporative either at ambient temperatures and pressures or at elevated temperatures used in processing to prepare the gel-adhesive composite. Non-volatile swelling agents allow the gel to remain a gel after processing and during use, preserving the swollen condition of the hydrocolloid for its high moisture vapor transmission properties.

Thus, gel-adhesive composite of the present invention retains the high peel adhesion and high shear adhesion properties of the pressure sensitive adhesive in

-6-

the presence of moisture vapor and other fluids because the high moisture vapor transmission rate property provided by the gel facilitates removal of the moisture or other fluid from the area where the composite is  
5 adhered.

The gel-adhesive composite requires at least the pressure sensitive adhesive and the gel of hydrocolloid and swelling agent. Without the pressure sensitive adhesive, the gel may not be strong enough as  
10 an adhesive to provide continued adhesion in dry or moist skin conditions. Without the hydrocolloid, no gel can form, and the hydrophilic swelling agent would "bloom" to the surface of the adhesive, thus severely degrading adhesion. Without the swelling agent, the unswollen  
15 hydrocolloid in the adhesive may greatly reduce continued dry stick adhesion capability.

The gel-adhesive composite may also include a broad spectrum antimicrobial agent therein to provide medicinal treatment while the composite is adhered to the  
20 skin of the patient.

The composite may be coated on a backing material or web also preferably having a high moisture vapor transmission rate to provide strength to the composite and protection from exposure of the skin of the patient to the surrounding environment. The composite  
25 resists the loss of adhesion to skin when exposed to moisture, water, exudate, or other fluid present in or about the skin or the skin opening.

13. A method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate,  
30 comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel  
35 particles;

(b) dispersing said gel particles into a hydrophobic solution comprising a pressure sensitive adhesive;

5 One method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix comprises swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel particles, and dispersing said gel particles into a hydrophobic solution comprising a pressure sensitive adhesive, coating said solution on a release liner, and drying said solution to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

10 15 Alternatively, the gel and the adhesive may be mixed in a latex solution. That method comprises swelling a hydrocolloid with a non-volatile swelling agent compatible with said hydrocolloid to form swollen hydrocolloid gel particles, dispersing said gel particles into a latex mixture comprising a pressure sensitive adhesive, coating said latex mixture on a release liner, and drying said mixture to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

20 25 Whether prepared using a hydrophobic solution or a latex mixture, any solvents used in preparing the gel and/or the pressure sensitive adhesive are removed, principally by evaporation, to yield the gel-adhesive composite.

30 35 The gel-adhesive composites of the present invention are achievements of the balancing of two important properties for medical adhesives involving the adhering of a material to the skin or skin opening: (1) significant adhesive strength in dry or moist conditions continuously for an extended period which does not exhaust itself upon initial swelling of hydrocolloidal material, and (2) a high moisture vapor transmission

-8-

rate. The composites of the present invention bridge the gap between high moisture vapor transmission rates provided by hydrogels and significant adhesive strength provided by conventional pressure sensitive adhesives.

5 Consequently, balancing these properties permits the composites of the present invention to provide utility for a wide variety of skin adhesive applications. Nearly transparent composites have great utility as incise drapes, dressings, bandages, tapes of  
10 all varieties for use on skin, and other skin contacting uses.

#### Brief Description Of The Drawing

FIG. 1 is a cross-section of a typical coating  
15 of the gel-adhesive composite of the present invention on a backing material, showing in the coating the dispersion of the gel throughout the pressure sensitive adhesive matrix.

20 FIG. 2 is a tri-coordinate graph depicting various ranges of weight fractions of pressure sensitive adhesive, hydrocolloid, and swelling agent used to prepare a gel-adhesive composite within the scope of the present invention.

25 Embodiments Of The Invention

#### THE GEL-ADHESIVE COMPOSITE

The gel-adhesive composite of the present invention comprises a two phase system. When used in medical applications, the composite adheres to the surface of the skin of the patient and maintains that surface in as dry an environment as can occur where the skin or skin opening exudes perspiration, or other body fluids.

#### THE PRESSURE SENSITIVE ADHESIVE

In medical application, the pressure sensitive adhesive must be tacky at room temperature as well as at skin temperature of patients. Also, the adhesive must be 5 dermatologically acceptable, i.e., after continuous contact with skin, there is little adhesive residue upon removal and there is no significant reaction with skin during adhesion.

The strength of the pressure sensitive adhesive phase of the composite depends on the type of pressure 10 sensitive adhesive chosen. The adhesives must provide sufficient adhesive strength to adhere the gel-adhesive composite to the skin of the patient.

The pressure sensitive adhesives may be 15 polymeric adhesive compositions prepared from a combination of monomers, homopolymers, copolymers and tackifiers, or blends thereof to produce polymeric adhesive compositions containing polyacrylates, polyolefins, silicone adhesives, natural or synthetically derived rubber base adhesives, or polyvinyl ethers.

Preferably, the pressure sensitive adhesives useful in the composite are hydrophobic allowing the adhesives of the pressure sensitive adhesive to resist absorbing either hydrophilic swelling agent from the dispersed gel or moisture or other body exudate gathering 25 at the skin or skin opening during use. The composite retains its strong adhesiveness even in the presence of water and swelling agents since the pressure sensitive adhesive is unaffected and not plasticized by these agents. Excess moisture is taken away from the skin 30 surface by the gel having a high moisture vapor transmission rate. This prohibits adhesion loss due to pooling of moisture under the adhesive against the skin.

The pressure sensitive adhesive optimally 35 should not absorb any swelling agent and preferably less than 0.5 weight percent of its weight. It has been found that the pressure sensitive adhesive may absorb swelling

-10-

agent in amounts up to 5 weight percent of its weight in certain circumstances without overly plasticizing the pressure sensitive adhesive.

Preferred adhesives are acrylic  
5 pressure-sensitive adhesive copolymers comprising "A" and "B" monomers as follows: Monomer A is a hydrophobic monomeric acrylic or methacrylic acid ester of alkyl alcohol, the alkyl alcohol containing 4 to 10 carbon atoms, preferably 6 to 10 carbon atoms, more preferably 6  
10 to 8 carbon atoms, and most preferably 8 carbon atoms.

Examples of suitable A monomers are n-butyl, n-pentyl, n-hexyl, isoheptyl, n-nonyl, n-decyl, isohexyl, 2-ethyloctyl, isoctyl and 2-ethylhexyl acrylates. The most preferred monomer is isoctyl acrylate.

15 Monomer B is a reinforcing monomer comprising acrylic acid; methacrylic acid; alkyl acrylates and methacrylates containing 1 to 3 carbon atoms in the alkyl group; acrylamide; methacrylamide; lower alkyl-substituted acrylamides (i.e., the alkyl group containing 1 to 4 carbon atoms) such as tertiary-butyl acrylamide; diacetone acrylamide; N-vinyl-2-pyrrolidone; vinyl ethers such as vinyl tertiary-butyl ether; substituted ethylenes such as derivatives of maleic anhydride, dimethyl itaconate and monoethylformate; or  
20 vinyl perfluoro-n-butyrate. The preferred B monomers are acrylic acid, acrylamide and N-vinyl-2-pyrrolidone. The most preferred B monomer is N-vinyl-2-pyrrolidone.

The A monomer in such copolymer is present in the pressure sensitive adhesive copolymer in an amount by weight of about 85 to 98 percent by weight, and  
30 preferably about 90 to 98 percent by weight of the weight of all monomers in the copolymer.

The B monomer in such a copolymer is present in the pressure sensitive adhesive copolymer in an amount by weight of about 2 to about 15 percent by weight, and  
35 preferably about 2 to 10 percent by weight of the weight of all monomers in the copolymer.

Most preferably, the pressure sensitive adhesive of the present invention is an isoocetyl acrylate/N-vinyl pyrrolidone copolymer in a weight fraction ratio of 91:9.

5           The adhesive copolymers of the above type are known and their method of preparation is well known to those skilled in the art, having been described for example, in U.S. Patent RE 24,906 of Ulrich. Since the pressure sensitive adhesives described above are inherently rubbery and tacky and are suitably heat and light stable, there is no need to add tackifiers, crosslinkers, or stabilizers. However, such may be added if desired.

10           The availability and preparation of other pressure sensitive adhesives useful in the present invention are described in the literature. In the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., Satas, Editor, (Von Nostrand Reinhold, New York 1989), a number of types of useful pressure sensitive adhesives are discussed: natural rubber adhesives; A-B-A block copolymers, (such as polystyrene-polybutadiene-polystyrene (S-B-S), polystyrene-polyisoprene-polystyrene (S-I-S), polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S), and polystyrene-poly(ethylene/propylene)-polystyrene (S-EP-S) polymers); butyl rubbers and polyisobutylene; vinyl ether polymers; silicones; polyisoprene; butadiene acrylonitrile rubber; polychloroprene; atactic polypropylene; and additional descriptions of acrylic adhesives and acrylic dispersions. Any of these pressure sensitive adhesives may form the polymeric matrix into which the gel may be dispersed.

15           Desirably among these available pressure sensitive adhesives, silicone pressure sensitive adhesives (such as those disclosed in U.S. Patent

-12-

4,039,707) and polystyrene-polyisoprene-polystyrene A-B-A block copolymers (such as those disclosed in U.S. Patent 3,935,338) are useful.

5           THE GEL OF HYDROCOLLOID AND SWELLING AGENT

The gel of the gel-adhesive composite is hydrophilic to the extent necessary to maintain a dispersion of gel particles in the pressure sensitive adhesive matrix. At the surface of and throughout the 10 composite, the gel particles provide the mechanism to remove the moisture or other body exudate from the skin or skin opening. While the gel may have its own pressure sensitive adhesive properties, it is not necessary. The adhesive matrix provides the necessary adhesiveness which 15 is maintained by the gel's moisture vapor transmission properties.

The gel in the gel-adhesive composite comprises the hydrocolloid solid and the swelling agent liquid. The ratio of these two constituents of the gel is 20 important to the functioning of the composite. The ratio of the swelling agent to the hydrocolloid and the ratio of the gel to the adhesive provide the basis for balancing the adhesive and moisture vapor transmitting properties of the composite.

25

THE HYDROCOLLOID

The hydrocolloid used in the present invention may be any synthetically prepared or naturally occurring polymer capable of forming a thickened gel in the 30 presence of the swelling agent. Varieties of hydrocolloids within the scope of the present invention include synthetic polymers prepared from single or multiple monomers, naturally occurring hydrophilic polymers or chemically modified naturally occurring 35 hydrophilic polymers.

-13-

Non-limiting examples of such hydrocolloids include polyhydroxyalkyl acrylates and methacrylates, polyvinyl lactams, polyvinyl alcohols, polyoxyalkylenes, polyacrylamides, polyacrylic acid, polystyrene sulfonates, natural or synthetically modified polysaccharides, alginates, xanthan gums, guar gums, and cellulosics.

When used in medical applications, the hydrocolloid must also be dermatologically acceptable and non-reactive with the skin of the patient or other components of the gel-adhesive composite including any antimicrobial agents which may be present in the composite.

Desirably, the hydrocolloid is a synthetic polymer which may be either linear or crosslinked. Non-limiting examples of synthetic hydrocolloids include polymers prepared from N-vinyl lactams, e.g. N-vinyl-2-pyrrolidone, 5-methyl-N-vinyl-2-pyrrolidone, 5-ethyl-N-vinyl-2-pyrrolidone, 3,3-dimethyl-N-vinyl-2-pyrrolidone, 3-methyl-N-vinyl-2-pyrrolidone, 3-ethyl-N-vinyl-2-pyrrolidone, 4-methyl-N-vinyl-2-pyrrolidone, 4-ethyl-N-vinyl-2-pyrrolidone, N-vinyl-2-valerolactam, and N-vinyl-2-caprolactam.

Other monomers useful to prepare a synthetic hydrocolloid include hydroxyalkyl acrylates and methacrylates, (such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate), acrylic acid, methacrylic acid and a tertiary amino-methacrylimide, (e.g. trimethylamino-methacrylimide), crotonic acid, and pyridine.

Other monomers useful to prepare a synthetic hydrocolloid include water soluble amides, (such as N-(hydroxymethyl)acrylamide and -methacrylamide,

N-(3-hydroxpropyl)acrylamide, N-(2-hydroxyethyl) methacrylamide, N-(1,1-dimethyl-3-oxabutyl)acrylamide N-[2-(dimethylamine)ethyl]acrylamide and -methacrylamide, N-[3-(dimethylamino)-2-hydroxylpropyl]methacrylamide, and  
5 N-[1,1-dimethyl-2-(hydroxymethyl)-3-oxabutyl]acrylamide); water-soluble hydrazine derivatives, (such as trialkylamine methacrylimide, and dimethyl-(2-hydroxypropyl)amine methacrylimide); mono-olefinic sulfonic acids and their salts, (such as sodium ethylene sulfonate, sodium styrene sulfonate and 2-acrylamido-2-methylpropanesulfonic acid); and the following monomers containing nitrogen in the non-cyclic or cyclic backbone of the monomer: 1-vinyl-imidazole, 1-vinyl-indole, 2-vinyl imidazole, 4(5)-vinyl-imidazole,  
10 15 2-vinyl-1-methyl-imidazole, 5-vinyl-pyrazoline, 3-methyl-5-isopropenyl-pyrazole, 5-methylene-hydantoin, 3-vinyl-2-oxazolidone, 3-methacrylyl-2-oxazolidone, 3-methacrylyl-5-methyl-2-oxazolidone, 3-vinyl-5-methyl-2-oxazolidone, 2- and 4-vinyl-pyridine,  
20 25 3-isopropenyl-pyridine, 2- and 4-vinyl-piperidine, 2- and 4-vinyl-quinoline, 2,4-dimethyl-6-vinyl-s-triazine, and 4-acrylyl-morpholine.

Other hydrocolloidal polymers, either naturally occurring or synthetically prepared, are useful in the present invention. These materials include polyvinyl alcohol, polyoxyalkylenes, and such naturally occurring or synthetically modified hydrocolloidal materials as polysaccharides, gums, and modified cellulosics.

30 Representative polysaccharides include starch, glycogen, hemicelluloses, pentosans, gelatin, celluloses, pectin, chitosan, and chitin. Representative gums include Arabic, Locust Bean, Guar, Agar, Carrageenan, Xanthan, Karaya, alginates, tragacanth, Ghatti, and Furcelleran gums. Representative modified celluloses include methyl cellulose, hydroxypropyl methyl cellulose, carboxymethylcellulose, and hydroxypropyl cellulose.

Crosslinking of the linear polymer chains of the hydrocolloid may be desired to improve cohesive properties of the gel dispersed in the pressure sensitive adhesive matrix. When such crosslinking is desired for polymers made from vinyl monomers discussed above, a multi-ethylenically unsaturated compound with the ethylenic groups being vinyl, allyl, or methallyl groups bonded to nitrogen, oxygen or carbon atoms can be used.

Non-limiting examples of crosslinking agents for vinyl containing polymers include divinyl, diallyl, or dimethallyl esters (e.g. ethylene glycol dimethacrylate, divinyl succinate, divinyl adipate, divinyl maleate, divinyl oxalate, divinyl malonate, divinyl glutarate, diallyl itaconate, diallyl maleate, diallyl fumarate, diallyl diglycolate, diallyl oxalate, diallyl adipate, diallyl succinate, diallyl azelate, diallyl malonate, diallyl glutarate, dimethallyl maleate, dimethallyl oxalate, dimethallyl malonate, dimethallyl succinate, dimethallyl glutarate, and dimethallyl adipate); divinyl, diallyl or dimethallyl ethers (e.g. diethyleneglycol divinyl ether, butane diol divinyl ether, ethylene glycol divinyl ether, ethylene glycol diallyl ether, diethylene glycol diallyl ether, butane diol diallyl ether, ethylene glycol dimethallyl ether, diethylene glycol dimethallyl ether, and butane diol dimethallyl ether); divinyl, diallyl or dimethallyl amides including bis(N-vinyl lactams), (e.g., 3,3'-ethylene bis(N-vinyl-2-pyrrolidone) and methylene-bis-acrylamide); and divinyl, diallyl and dimethallyl ureas.

Preferable crosslinking agents include ethylene glycol dimethacrylate, methylene-bis-acrylamide, diallyl maleate, and 3,3'-ethylidene bis (N-vinyl-2-pyrrolidone).

For n-vinyl lactams, the preferred crosslinking agents are diallyl maleate and 3,3'-ethylidene bis (N-vinyl-2-pyrrolidone).

For acrylates and methacrylates, the preferred crosslinking agents are ethylene glycol dimethacrylate and methylene-bis-acrylamide.

Preferred hydrocolloids for the present invention are linear or crosslinked polyvinyl lactams. 5 Of the polyvinyl lactams, N-vinyl-2-pyrrolidone is preferred.

When crosslinking is desired, such crosslinking agents as diallyl maleate or 3,3'-ethylene bis 10 (N-vinyl-2-pyrrolidone) may be used to crosslink such polyvinyl lactams generally and poly-N-vinylpyrrolidone particularly.

Preferably, the crosslinked hydrocolloid is poly-N-vinylpyrrolidone prepared from the reaction of 15 from about 97 to about 99.92 percent by weight of N-vinyl-2-pyrrolidone and from about .08 to about 3 percent by weight of 3,3'-ethylene bis N-vinyl-2-pyrrolidone. Most preferably, the 3,3'-ethylene bis N-vinyl-2-pyrrolidone comprises about 0.16 20 percent by weight of the poly-N-vinylpyrrolidone.

#### THE SWELLING AGENT

The swelling agent for the hydrocolloid may be a broad variety of liquids which are non-volatile or 25 non-evaporative in ambient climatic conditions, and which are also incompatible with or extremely insoluble in the pressure sensitive adhesive or its solvent(s). The swelling agent must also be capable of swelling the hydrocolloid chosen, in order to form the gel phase of 30 the composite of the present invention.

Non-volatility avoids evaporative loss of the swelling agent from the gel, thereby retaining the gel's moisture vapor transmission utility for continued periods. Non-volatility for the swelling agent is desired not only at room or body temperatures but also at 35 the elevated temperatures of processing which range from about 75°C to about 250°C. Because these non-volatile

swelling agents have humectant properties at room temperatures, it is better to characterize an acceptable minimum amount of non-volatility at elevated temperature. For example, acceptable swelling agents for the present invention are sufficiently non-volatile if less than 10 percent of a given volume evaporates after exposure to a temperature of 75°C for one hour.

Incompatibility avoids plasticization of the pressure sensitive adhesive by the swelling agent. No significant migration of the swelling agent into the pressure sensitive adhesive occurs because of their relative mutual insolubility. When the swelling agent is hydrophilic and the pressure sensitive adhesive preferably is hydrophobic, there is a continuous and strong tendency for phase separation.

Because the swelling agent is incompatible with the pressure sensitive adhesive, there is no significant migration of the swelling agent liquid from the gel phase into the adhesive matrix. A swelling agent compatible with the pressure sensitive adhesive would undesirably plasticize the adhesive, destroying its effectiveness as a skin adhesive.

Optimally, no swelling agent should migrate from the gel to the pressure sensitive adhesive matrix. Plasticization of the pressure sensitive adhesive is avoided if less than about 5 weight percent of swelling agent migrates into the pressure sensitive adhesive matrix. However, in no event should the weight fraction ratio of hydrocolloid to swelling agent exceed 3:1. Thus, depending on the weight fraction ratio of pressure sensitive adhesive to gel, up to about 5 weight percent of swelling agent can migrate into the pressure sensitive adhesive without harming the properties of the gel or the adhesive of the composite. But less than 2 weight percent is acceptable in most instances, with less than than 1 weight percent being desirable and less than 0.5 weight percent being preferred.

Varieties of non-volatile swelling agents within the scope of invention, which are incompatible with the pressure sensitive adhesives contemplated herein, include room temperature liquid polyols, (including polyhydric alcohols), such as glycerol, propylene glycol, poly(ethylene) glycol (having a molecular weight in the range of about 200 to about 600) and polypropylene glycol (having a molecular weight in the range of about 350 to about 1,000); room temperature solid polyols (including polyhydric alcohols), (such as sorbitol, erythritol, threitol, ribitol, arabinitol, xylitol, allitol, talitol, mannitol, glucitol, glactitol, iditol, pentaerythritol, heptitol, octitol, nonitol, decitol, and dodecitol), blended with a room temperature liquid polyol; monoanhydroalditols (such as styracitol, polyalitol, D-Fructose, 1,4 anhydro D-mannitol and 1,4 anhydro-D-glucitol) blended with a room temperature liquid polyol; monosaccharides (such as pentoses, hexoses, and heptoses) blended with a room temperature liquid polyol; and ether alcohols, such as poly(ethylene) glycol ether (having a molecular weight in the range of 600 to 20,000) and polypropylene glycol ether (having a molecular weight in the range of 1,000 to 5,000) blended with a room temperature liquid polyol.

Of these polyols, desirable swelling agents are glycerol, propylene glycol, polyethylene glycol (200-600 molecular weight) and sorbitol blended with glycerol. Because of its non-volatility and low-cost availability, glycerol is the preferred swelling agent.

Optionally, volatile solvents such as water and monohydric alcohols may be used to assist in the preparation of the gel by initiating the swelling of the hydrocolloids or in aiding the dispersion of the gel particles in a hydrophobic pressure sensitive adhesive matrix. Whether in a hydrophobic solution or in a suspension or emulsion, such processing volatile agents are not considered swelling agents of the present

-19-

invention. The extent of removal of these volatile solvents is dependant on the requirements of the product application. In addition, depending on the air tightness of the packaging of a product incorporating a composite of the present invention, the gel particles therein may absorb atmospheric moisture. This may also be more or less desirable again depending on the product application.

10                   INTERRELATED WEIGHT FRACTIONS OF GEL AND  
ADHESIVE AND WEIGHT FRACTION RATIO OF HYDROCOLLOID TO  
SWELLING AGENT

15                   To achieve a balance of pressure sensitive adhesive properties and gel properties, the weight fractions of gel and adhesive in the resulting composite are controlled. However, because of the broad scope of properties which may be balanced, the gel may be dispersed in an amount by weight of about 1 to 95 percent by weight of the combined weight of gel and adhesive in the composite.

20                   To achieve the proper gel properties in view of the weight fractions of the gel and the adhesive, the weight fractions of the hydrocolloid and the swelling agent are controlled using weight fraction ratios for them.

25                   The pressure sensitive adhesive may have a weight fraction of from about 5 to about 99 percent by weight of the gel-adhesive composite. Desirably, the weight fraction of the adhesive in the gel-adhesive composite ranges from about 20 to about 95 percent by weight. Preferably, the weight fraction of the pressure sensitive adhesive in the gel-adhesive composite is from about 25 to about 90 parts by weight.

30                   The hydrocolloid may have a weight fraction of from about 0.01 percent to about 72 percent of the gel-adhesive composite of the present invention. Desirably, the weight fraction of the hydrocolloid in the

-20-

gel-adhesive composite ranges from about 0.05 to about 48 percent. Preferably, the weight fraction of the hydrocolloid in the gel-adhesive composite ranges from about 0.50 to about 30 weight percent.

5       The swelling agent may have a weight fraction of from about 0.25 to about 95 percent by weight of the gel-adhesive composite. Desirably, the range of the weight fraction of the swelling agent in the composite depends on the weight fraction of the hydrocolloid in the  
10 composite.

15      Depending on the properties desired for the gel-adhesive composite, the range of weight fraction ratios for the hydrocolloid to the swelling agent can be from about 3:1 to about 1:99. At the ratio of about 3:1, there is sufficient swelling agent to achieve a soft and pliable gel suitable for maintaining the strong adhesiveness of the composite. At the ratio of about 1:99, there is sufficient hydrocolloid to prevent the swelling agent from migrating through the pressure  
20 sensitive adhesive and "blooming" to the surface of the composition, thereby destroying its adhesiveness.

25      Desirably, the ratio of weight fractions of the hydrocolloid to the swelling agent is from about 1.5:1 to about 1:19. Preferably, based on a balancing of the performance of the moisture vapor transmission rate of the gel with the adhesiveness of the adhesive in the composite, the ratio of the weight fractions of the hydrocolloid to the swelling agent is from about 1:1.5 to about 1:19.

30      FIG. 2, a tri-coordinate graph, provides a convenient depiction of the acceptable, desirable and preferable weight fraction ratios of the three necessary components of the gel-adhesive composite of the present invention. FIG. 2 also depicts the ranges of acceptable, desirable and preferable weight fraction ratios of the hydrocolloid and the swelling agent within the gel of the present invention.  
35

The area in FIG. 2 inside lines A, A<sup>1</sup>, and A<sup>2</sup> graphically depicts that the weight fraction of the pressure sensitive adhesive is from about 5 to about 99 percent, the weight fraction of the hydrocolloid is from about 0.01 to about 72 percent, and the weight fraction of the swelling agent is from about 0.25 to about 94 percent as adjusted for the ratios of the hydrocolloid to the swelling agent of from about 3:1 to about 1:99 (the slopes of the lines A and A<sup>2</sup>, respectively).

For example, a composite containing 20 percent by weight of the pressure sensitive adhesive, 60 percent by weight of the hydrocolloid, and 20 percent by weight of the swelling agent appears on line A and hence at the border of the acceptable area, where the ratio of the hydrocolloid to the swelling agent is 3:1. For example, a composite having 50 percent by weight of the pressure sensitive adhesive, about 1 percent by weight of the hydrocolloid, and about 49 percent by weight of the swelling agent is on line A<sup>2</sup> within the acceptable area, where the ratio of the hydrocolloid to the swelling agent is about 1:99.

A weight fraction of 60 percent for the pressure sensitive adhesive, 20 percent by weight of the hydrocolloid, and 20 percent by weight of the swelling agent yields a composite clearly within the area in FIG. 2 bounded by lines A, A<sup>1</sup>, A<sup>2</sup> where the ratio of the hydrocolloid to the swelling agent is 1:1.

The areas bounded by bordering lines B, B<sup>1</sup>, B<sup>2</sup> and B<sup>3</sup> and C, C<sup>1</sup>, C<sup>2</sup> and C<sup>3</sup> in FIG. 2 similarly identify the desirable and preferable weight fractions of the composites of the present invention, respectively. The example in the prior paragraph of the weight percent pressure sensitive adhesive:hydrocolloid:swelling agent ratio of 60:20:20 is also within the desired range of weight fractions bounded by lines B-B<sup>1</sup>-B<sup>2</sup>-B<sup>3</sup>, where the desired ratio of hydrocolloid to swelling agent of 1:1. But an adhesive:hydrocolloid:swelling agent ratio of

-22-

50:10:40 is only within the preferred area of weight percent ranges, bounded by lines C-C<sup>1</sup>-C<sup>2</sup>-C<sup>3</sup>, where the ratio of hydrocolloid to swelling agent is 1:4.

5 The bordering lines also demonstrate the desired and preferred hydrocolloid:swelling agent ratios. Line B<sup>1</sup> has a slope matching the hydrocolloid:swelling agent ratio of 1.5:1. Line B<sup>3</sup> has a slope matching the ratio of 1:19. Line C<sup>1</sup> has a slope matching the ratio of 1:1.5. Shorter Line C<sup>3</sup> has the same slope as the slope  
10 of longer Line B<sup>3</sup>, 1:19.

15 As stated previously, optimally no swelling agent in the gel should migrate into the adhesive matrix. Preferably less than 0.5 weight percent, and desirably less than 1 weight percent, of the adhesive matrix should comprise migrated swelling agent.

In no event should the amount of swelling agent remaining in the gel cause the hydrocolloid:swelling agent ratio to exceed about 3:1.

20 Further, in no event should the amount of swelling agent migrating into the adhesive matrix exceed 5 weight percent of the adhesive. This avoids plasticization of the adhesive and reduction of adhesive strength. Residuing of adhesive on the skin is also avoided.

25 The above constraints define the outer limits of tolerance of swelling agent migration. It is desirable to select swelling agents and pressure sensitive adhesives which are incompatible, to avoid reaching such outer limits. Such incompatibility of  
30 swelling agent and adhesive preserves the softness and moisture vapor transmission rate properties of the gel particles dispersed within the adhesive matrix for composites of all ratios of the present invention.

35

#### OPTIONAL COMPONENTS

The addition of a variety of biologically active materials into the gel-adhesive composite of the

present invention is desirable when the composite is placed in contact with the skin or skin opening of a patient. Bandages, tapes, dressings, drapes, and the like are all used in conditions where it is desirable to reduce bacteria levels to minimize infection risk or to treat the effects of infections at the skin or skin openings of a patient. For example, in the application of composites of the present invention as incise drapes, antimicrobial agents may be incorporated into the gel of the composition. Broad spectrum antimicrobial agents are disclosed in U.S. Patent No. 4,310,509.

Useful antimicrobial agents include a wide variety of agents which are compatible with both the gel and the pressure sensitive adhesive of the composite. These agents can be incorporated prior to polymerization or gelation of the hydrocolloid, provided they do not interfere with such reaction(s). Alternatively, the agents can be incorporated after polymerization of the hydrocolloid, if any. In the latter case, the antimicrobial agents are dissolved or dispersed in either non-volatile swelling agent or volatile solvent.

Examples of antimicrobial agents are numerous, but desirably such antimicrobial agents as parachlorometaxylenol; chlorhexidine and its salts such as chlorhexidine acetate and chlorhexidine gluconate; iodine; iodophors; poly-N-vinylpyrrolidone-iodophors; silver oxide, and silver and its salts, and antibiotics (e.g., neomycin, bacitracin, and polymyxin B) are useful in accordance with the present invention.

The antimicrobial agents may be included in the composites in a weight from about 0.01 percent to about 10 percent by weight of the total composite after the weight percents of the adhesive, hydrocolloid and swelling agent are determined.

Other additives may be incorporated into the composite to enhance the physical properties of the adhesive and the antimicrobial properties of the

composite containing an antimicrobial agent. For example, iodates and iodides may be added to enhance the solubility of the iodine antimicrobial agent during the introduction of the antimicrobial agent into the gel and 5 to adjust the free iodine in the composite.

Photoinitiators, and other catalysts may be used in the polymerization processes for the pressure sensitive adhesive and in the polymerization or gelation of the hydrocolloid.

10 Compounds to buffer the pH of the composite may be added to provide a non-irritating pH for use with sensitive skin tissue or to otherwise maximize antimicrobial activity.

15 Further, the incorporation of a surfactant into the composite may improve antimicrobial activity in or at the skin of the patient.

#### PREPARATION OF THE GEL-ADHESIVE COMPOSITE

There are two methods currently known for the 20 preparation of the composite of the present invention. Both methods involve the separate preparation of the pressure sensitive adhesive and the gel following by the mixing and drying of them to form the composite.

One method involves mixing the gel either with 25 or without a hydrophilic solvent into an adhesive in bulk or in a volatile solvent. The other method involves mixing the gel into a latex adhesive with volatile hydrophilic solvent or solvents.

When the method used involves gel particles 30 mixed into an adhesive in bulk or in a volatile, hydrophobic solvent, the gel particles must be dispersed into the adhesive. Equipment such as a "Laboratory Dispersator, Series 2000, Model 84" mixer, commercially available from Premier Mill Corporation of Reading, Pennsylvania may be used for solution preparation. A 35 Banbury mixer could be used for bulk preparation. The process of mixing should continue until the gel particles

are fully dispersed in the adhesive. Then, the mixing is stopped to allow for the removal of any bubbles created during the mixing process. The mixing process may occur at ambient temperatures and pressures.

5 When the composite is prepared by mixing the gel particles into a latex solution of the hydrophobic pressure sensitive adhesive, the mixing may be accomplished by using the "Laboratory Dispersator" mixer described above. The mixing process may occur at ambient  
10 temperatures and pressures. The mixing should continue until the gel particles are fully dispersed. Then the mixing is stopped to allow for the removal of any bubbles created during the mixing process.

15 Regardless of the method of preparation, whenever a volatile solvent for the pressure sensitive adhesive, the gel, or both is present during the final mixing, it/they must be removed, generally by application of heat or other drying mechanism. As drying occurs, the adhesive forms a nearly continuous matrix with the gel  
20 particles dispersed therein. The temperatures of evaporating the volatile solvent(s) without adversely affecting the remaining adhesive and gel depends upon the type of volatile solvent(s) employed. Generally, however, the mixture is dried at temperatures between  
25 about 75°C and about 250°C.

30 The resulting composite may be spread or coated onto a release liner and dried to form films having thicknesses of from about 10 to about 1,000 microns and desirably from about 20 to about 100 microns. Thereafter, depending on the desired application, the layer of composite may be applied to a backing material by laminating.

35 In elevated temperature preparations, the composite can endure temperatures in excess of 100°C without chemical or physical deterioration. If a biologically active material such as an antimicrobial

agent is included in the composite, the temperature of the drying of the composite and its lamination to a backing material should not exceed 100°C.

5 PREPARATION OF THE PRESSURE SENSITIVE ADHESIVE

The preparation of the pressure sensitive adhesive depends on the type of adhesive, the type of polymerization (e.g., addition or condensation), and the polymerization technique (e.g., bulk, solution, 10 suspension or emulsion polymerization).

The pressure sensitive adhesive polymerization technique chosen is selected from conventional polymerization technique(s) known for a particular pressure sensitive adhesive. Sources of polymerization preparation techniques include Organic Polymer Chemistry, K.J. Saunders, Chapman and Hall (Halsted Publishing, New York, 1973), Applied Polymer Science, R. W. Tess and G. W. Poehlein, American Chemical Society (American Chemical Society, Washington, D.C., 1981), and Principles of Polymerization, George Odien, Wiley-Interscience (John Wiley and Sons, New York, 1981), and the Handbook of Pressure Sensitive Adhesive Technology, 2nd Ed., supra. 15 20

For example, acrylic pressure sensitive adhesives may be prepared according to U.S. Patent RE 24,906. When prepared by solution polymerization, the monomers are soluble in solvents, commonly ethyl acetate, cyclohexane, toluene, and n-heptane. The polymer is also usually soluble in the solvent allowing a pure polymer to be coated onto a surface and then dried. When prepared by emulsion polymerization, the latex of water-insoluble polymers in water maintains a phase separation until removal of the water. 25 30

Pressure sensitive adhesives may be prepared by solution polymerization from A-B-A block copolymers, natural rubber, styrene-butadiene, polyisoprene, butyl rubber, polyisobutylene, polychloroprene, and blends 35

thereof. Pellets of the commercially available polymer are mixed into a solvent and heated in the presence of tackifiers and often plasticizers, in order to develop a non-rigid polymer having the requisite tack. Chapters 5 11, 13, 14, and 19 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., referenced above, discusses the choices of materials and methods of preparation. A frequently used tackifier is polyterpene resin.

10 The rubber based adhesives may also be prepared in a latex. For example, styrene and butadiene may be dispersed in water with an emulsifier (such as sodium alkyl benzene sulfonate) and an initiator (such as potassium persulfate). Polymerization occurs typically anaerobically with mixing for about 16-24 hours at 60°C. 15 Chapter 12 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, describes such latex preparation processes.

20 Silicone pressure sensitive adhesives are usually commercially supplied in a hydrocarbon solvent. Upon evaporation, the silicones exhibit pressure 25 sensitive adhesive properties. As described in Chapter 18 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, a catalyst (such as an organic peroxide, an amino silane, or a metal salt of an organic acid) is added to reinforce the silicone network, increasing cohesiveness.

30 The polymerization of vinyl ether homopolymers may be carried out by batch processing, or continuous processing in bulk or in solution. Whichever processing is used, cationic initiators such as  $\text{BF}_3$ , or  $\text{AlCl}_3$ , are present. Copolymers of vinyl ethers and acrylates are polymerized by free radical emulsion polymerization in water with potassium peroxodisulfate. Chapter 17 of the 35 Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, describes the polymerization.

If volatile solvents are necessary or desirable for the preparation of the pressure sensitive adhesive, such solvents should be hydrophobic and generate phase separating regions when encountering the gel particles having hydrophilic swelling agents therein or volatile hydrophilic solvents used to prepared the gel.

Desirably, hydrophobic volatile solvents for the pressure sensitive adhesive are aliphatic or aromatic hydrocarbons, such as heptane, toluene, xylene, and the like and blends containing other miscible solvents such as ethyl acetate.

#### PREPARATION OF THE GEL

The preparation of the gel involves the mixing or swelling of finely divided particles of the hydrocolloid with the swelling agent and optionally a volatile solvent or solvents compatible or miscible with the swelling agent but incompatible with the adhesive.

The preparation of the gel occurs after preparation of the hydrocolloid and its separation into finely divided particles. A swelling agent is then added in amounts sufficient to achieve the desired weight fraction ratio. The swelling agent swells the hydrocolloid prior to any mixing with the adhesive, such that the swollen gel particles are fully formed prior to being dispersed in the pressure sensitive adhesive matrix.

Swelling may occur at ambient or elevated temperatures (up to 100°C) and ambient pressures in a mixing vessel with simple hand mixing or stirring. The swelling may occur in the presence of such volatile, hydrophilic solvents as water, ethanol, methanol and other monohydric alcohols. However, to the extent possible, it is desirable to swell the hydrocolloid without volatile solvents to avoid the subsequent efforts to remove the solvent to form the composite.

## PREPARATION OF THE HYDROCOLLOID

The preparation of the hydrocolloid depends on the choice of hydrocolloid used. If the hydrocolloid is naturally occurring then it is used directly. If the hydrocolloid is synthetic or synthetically modified from a naturally occurring material, the synthesis may be by a variety of methods including condensation polymerization or addition polymerization from monomeric units. The choice of hydrocolloid polymerization technique may be selected based on the hydrocolloid in reference to conventional polymerization technique(s) known for that hydrocolloid. Sources of polymerization preparation techniques include Organic Polymer Chemistry, K.J. Saunders, Chapman and Hall, Applied Polymer Science, R. W. Tess and G. W. Poehlein, American Chemical Society, and Principles of Polymerization, George Odien, Wiley-Interscience, supra.

Desirably, a free radically polymerized hydrocolloid is prepared by photochemically activated polymerization. The monomer, desirably also a crosslinking agent, and the photoinitiator can be polymerized in bulk or in a hydrophilic solution of the swelling agent alone or with other hydrophilic solvents which may be volatile. The precursor can be coated on a flat surface and irradiated with ultra-violet light. Optionally, the hydrocolloid can be ground into particles, emulsified in a volatile solvent and reprecipitated to remove any unreacted monomer, and then dried and ground into a fine powder.

Photoinitiators available for use are well known and have been described in the polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley and Sons (1966) and in Progress in Organic Coatings, 13 (1985) 123-150. Representative examples of such initiators include acyloins and related compounds such benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl

ether, alpha-methylbenzoin, and  
2-hydroxy-2-methyl-1-phenyl-1-propanone; and benzilketals  
such as benzildimethylketal and benzildiethylketal. A  
presently preferred photoinitiator is  
5 2-hydroxy-2-methyl-1-phenyl-1-propanone.

Generally, the photoinitiator is used in  
amounts ranging from about 0.01 to about 5 percent by  
weight of monomer. Preferably, about 0.02 to 2 percent  
by weight of photoinitiator is used. When the activating  
10 energy is ultraviolet light, the irradiation is typically  
initiated at a temperature in the range of 0°C to 50°C  
for 0.5 minutes to 5 hours or more depending upon the  
intensity of the radiation.

When poly N-vinylpyrrolidone is the  
15 hydrocolloid chosen, polymerization may take place in  
solution, bulk, or suspension. When  
N-vinyl-2-pyrrolidone is polymerized in a hydrophilic  
solution of a solvent and/or the swelling agent, the  
solids achieved are swollen gel particles which may be  
20 ground into fine particles. Desirably, the swelling  
agent may serve as the solvent.

When the polymerization of  
N-vinyl-2-pyrrolidone is in bulk, a hard polymer is  
obtained which must also be ground into fine particles  
25 prior to swelling such particles with the swelling agent.

However obtained, the hydrocolloid particles  
are swollen with the swelling agent to yield soft and  
pliable gel particles. As described above, the swollen  
gel particles are dispersed into the adhesive solution  
30 using a high shear grinder or mixer to physically  
randomly disperse the gel particles of various dimensions  
into the pressure sensitive adhesive matrix.

#### USEFULNESS OF THE GEL-ADHESIVE COMPOSITE

Referring to FIG. 1, the usefulness of the  
35 composite may be seen. The gel-adhesive layer 10  
comprises a plurality of discrete gel particles 30

dispersed in the continuous matrix of the pressure sensitive adhesive 20. The layer 10 is contacting both a layer 40 of backing material and a release liner 50.

5 The discrete gel particles 30 are of various sizes and are dispersed randomly in the adhesive 20. The variety of sizes depends on the size of the hydrocolloid particle prior to swelling and gel break-up during dispersive mixing or shearing. Desirably, the particles 30 range from about 1 micron to about 600 microns.

10 The composite of the present invention may be coated onto a variety of webs or backing materials 40, including films, substrates, or other elastic, porous or breathable woven or nonwoven materials useful in medical applications. A release liner 50, typically a silicone 15 release liner, protects the other exposed surface of the coated layer 10.

20 In such manner, the release liner 50 is removed and the layer 10 of composite may be applied to the skin of the patient as a part of a medical tape, a surgical drape, an incise drape, a wound dressing, a bandage of general medicinal utility, or other medical device. The adhesiveness of the pressure sensitive adhesive combined 25 and balanced with the high moisture vapor transmission rate properties of the gel permits wide utility in medical applications.

The composite layer 10 may be coated on a layer 40 of any of several backing materials also having a high moisture vapor transmission rate for use as medical tapes, dressings, drapes, bandages, and the like. 30 Suitable backing materials include those disclosed in U.S. Patents 3,645,835 and 4,595,001. Other examples of a variety of films commercially available as extrudable polymers include "Hytrel<sup>R</sup> 4056" and "Hytrel<sup>R</sup> 3548" branded polyester elastomers available from E.I. DuPont de Nemours and Company of Wilmington, Delaware, "Estane" 35

branded polyurethanes available from B.F. Goodrich of Cleveland, Ohio or "Q-thane" branded polyurethanes available from K.J. Quinn & Co. of Malden, Massachusetts.

5       The layer 10 combined with a layer 40 of suitable backing material may be used as a surgical drape, and particularly an incise drape. Suitable backing materials are disclosed in U.S. Patents 4,627,427 or 3,809,077, to be used for incise drapes or surgical drapes, respectively.

10      When used as an incise drape, the composite may be used with a film prepared from "Hytrel 4056" branded polyester elastomer available from DuPont as the backing material.

15      The composite layer 10 can be coated on the backing layer 40 by a variety of processes, including, direct coating, lamination, and hot lamination. The backing layer 40 may also be a release liner onto which the composite is coated prior to drying.

20      The method of applying the composite to the release liner involves the same coating process as that described above for the preparation of the composite after the drying step. The methods of lamination and hot lamination involve the application of pressure, or heat and pressure, respectively, on the layer of composite 25 layer 10 to the backing material layer 40. The temperature for hot lamination ranges from about 50°C to about 250°C, and the pressures applied to both lamination and hot lamination range from 0.1 Kg/cm<sup>2</sup> to about 50 Kg/cm<sup>2</sup>.

30      The balance of adhesive and moisture vapor transmission properties desired can depend on the climatic conditions where the composite may be used. Diaphoretic patients or patients in intemperate climates where perspiration is unwanted but constantly present may 35 use composites which emphasize high moisture vapor transmission rates over the adhesiveness of the tape, bandage, or dressing used. Conversely, in temperate

climates or even in the chilled conditions of modern operating rooms, the composites which emphasize strong adhesives for use as incise drapes and which have near transparency and continuously good moisture vapor transmission of body fluids are needed.

5           High moisture vapor transmission rates of the composite encourage a rate of moisture withdrawal from the surface of the skin which thereby attempts to maintain dry skin conditions under the tape, dressing, 10 drape and the like. The adhesive matrix thus remains adhered. In addition to maintaining continued good adhesion, low skin or wound moisture levels reduce the risk of infection.

15           As described above, optionally, the composite may contain an antimicrobial agent in gel-adhesive layer 10 help reduce infection at the skin or skin opening.

20           While FIG. 1 and various examples appearing below have described the use of the composite with a backing web or substrate, the scope of the invention is not so limited. There are circumstances where a backing 25 layer would not be desired and the adhesive would be used as a coating alone on the skin or skin opening. Examples of uses of the coating alone include the use of the composite to hold two pieces of skin tissue together or the composite to hold a liquid absorbing material, such as gauze, in contact with the skin.

30           While the composites of the present invention have particular utility in the medical or veterinary applications, the utility of the composites is not so limited. A wide variety of adhesive composites having continuous moisture vapor transmission capability may be used for application to inanimate objects which must be kept dry notwithstanding a continuing exuding of moisture or water. The securement of a tape to repair torn 35 material exposed to wet environments, such as a tent, may be aided by the use of the composite of the present

invention because the moisture vapor transmission rate of the tape will attempt to provide continued dry stick adhesion.

5 PROPERTIES OF THE GEL-ADHESIVE COMPOSITE

Referring again to FIG. 1, the gel particles 30 dispersed in the continuous adhesive matrix 20 provide the means by which moisture at the skin is continuously removed by diffusion of moisture through the gel-adhesive 10 layer 10.

While not being bound to any particular theory, it is believed that the swelling of the hydrocolloid with the non-volatile swelling agent at weight fraction ratios from 3:1 to 1:99 prior to mixing of the gel with the 15 adhesive provides a high diffusion rate environment for moisture and antimicrobial to rapidly diffuse through the gel. By comparison, the hard, unswollen hydrocolloid particles in stoma-type adhesives have very low diffusion rates and require swelling of the hydrocolloid by 20 moisture prior to providing high moisture or antimicrobial agent diffusion through that type of adhesive.

Thus, the gel particles 30 more quickly and 25 more efficiently transport the moisture from the skin because the gel particles 30 are already in a swollen equilibrium before any contact with the wet or moist environment of the skin. Because the swelling agent is non-volatile, the equilibrium is maintained both before the composite is used and during use in contact with 30 skin. The volatile moisture is transmitted, not the non-volatile swelling agent. These particles 30 attempt to continuously dry an otherwise wet environment by the transmission of moisture from the skin or the skin opening while the adhesive matrix 20 maintains adhesion.

In addition to the interrelated weight 35 fractions of the pressure sensitive adhesive, the hydrocolloid, and the swelling agent and the ratio of the

hydrocolloid to the swelling agent, it is important for the present invention to have gel particles 30 in the composite 10 which are very soft and pliable. If the particles 30 are not soft and pliable, the particles begin to become reinforcing materials in the adhesive matrix 20, stiffening the gel-adhesive composite layer 10 and diminishing the composition's adhesiveness.

The soft and pliable gel particles 30 permit the adhesive matrix 20 of the gel-adhesive composite layer 10 to continue to adhere to the skin in those regions where the gel particles 30 do not contact the skin.

Shear modulus is a measurement of the softness and pliability desired for the gel of the present invention. Generally the shear modulus of the gel particles 30 should be less than  $6.2 \times 10^6$  dynes/cm<sup>2</sup>.

A desirable upper limit for the shear modulus of the gel of the present invention is  $1.5 \times 10^5$  dynes/cm<sup>2</sup>. A more preferred maximum of shear modulus for the gels of the composites of the present invention is  $4.2 \times 10^4$  dynes/cm<sup>2</sup>.

As is known to those skilled in the art, the shear modulus upper limit of  $6.2 \times 10^6$  dynes/cm<sup>2</sup> represents an extremely soft material compared with other elastomers known to those skilled in the art.

The balance of the high moisture vapor transmission rate and the continued adhesive properties for that composite are also influenced by the particle size of the gel particles 30 in the adhesive matrix 20. It is axiomatic that smaller particles offer a larger surface area to volume ratio, which helps increase moisture vapor transmission. But it has also been noted that particle sizes for the gel which approximate the thickness of layer gel-adhesive composite 10 of the composite are believed to act as a pore in the matrix of the adhesive, thereby also increasing the moisture vapor transmission rate.

Thus, a wide range of particle sizes may yield acceptable gel-adhesive composite results. A range of particle size for the gel particles 30 of from about 1 to about 600 microns is acceptable, while a range of 5 particle size of from about 25 to about 100 microns is desirable.

The gel particles 30, soft, in swollen equilibrium and of various sizes dispersed in the adhesive matrix 20, can provide to the layer 10 a 10 significantly higher moisture vapor transmission rate than the same adhesive without a gel dispersed therein. The amount of increase depends on the amount of gel dispersed in the adhesive matrix and the size of the gel 15 particles so dispersed. One may increase the moisture vapor transmission rate property of an adhesive by dispersing gel particles therein. Also, one may improve adhesion with a thicker adhesive layer in a medical article while maintaining the moisture vapor transmission rate property of the original thickness of adhesive by 20 dispersing gel into the thicker adhesive matrix. Thus, the moisture vapor transmission rate properties of a gel-adhesive composite of the present invention can be tailored to the use for the composite.

For example, it has been found with acrylate 25 adhesives having as little as 10 weight percent of poly(N-vinyl lactam) particles swollen with glycerol, displays a 20 percent increase in the moisture vapor transmission rate. When there are substantial weight fractions of gel in the composite, for example, between 30 50 and 75 weight percent, the moisture vapor transmission rates can be as much as 200 to 700 percent greater than the pressure sensitive adhesive displays.

The high moisture vapor transmission rates achieved by the gel of the composite do not adversely 35 impact the adhesion strength of the pressure sensitive adhesive. Initially, short term (a few hours), and long term (24 hours) adhesion values of the gel-adhesive

composites having a broad range of gel concentrations follow the adhesion values of the pressure sensitive adhesive over the same periods. For example, in a preferred embodiment of poly (N-vinylpyrrolidone) hydrocolloid in glycerol swelling agent, the gel comprising 25 percent by weight of the composite, where the ratio of hydrocolloid to swelling agent was 1:1, the skin adhesion of the composite after 24 hours was nearly as great as the skin adhesion for the pressure sensitive adhesive alone after 24 hours.

Further, the gel-adhesive composites display excellent wet adhesion properties making the composite equally attractive to patient care conditions where dry skin environments become wet or where wet skin environments must be made drier.

The peel adhesive strength of the composites of the present invention are strong notwithstanding the presence or absence of humidity. For example, in a composite having about 75 percent by weight of an acrylate pressure sensitive adhesive and about 25 percent by weight of poly (N-vinyl lactam) gel, within which the lactam hydrocolloid to glycerol swelling agent ratio was about 0.43:1, the T-Peel adherence to low density polyethylene (LDPE) (which is used to simulate skin adhesion) at dry or humid conditions was better than the adhesiveness of the acrylate pressure sensitive adhesive alone. The humid LDPE test at 50 percent relative humidity shows a result which was even greater than the dry LDPE T-Peel adhesive strength.

Thus, the range of adhesive strength retained by the gel-adhesive composite may exceed the adhesive strength of the adhesive alone and at the very least ranges from about 40% to about 500% of the adhesive strength of the adhesive alone.

A useful feature of the gel-adhesive composites of the present invention is the apparent near transparency of the composite, notwithstanding the two

phase nature of that composition. Because the gel and the pressure sensitive adhesive may be chosen from candidates having nearly identical indices of refraction, it is possible to achieve an at least nearly transparent composite. A nearly transparent composite enables the practitioner to use this coating as an adhesive for incise drapes or for other purposes which call for translucency approaching transparency. An incision area must be seen through the adhesive, and a composite of the present invention provides significantly improved utility over other adhesives.

While not being bound to any particular theory, it is believed that the near transparency of the composites of the present invention is directly related to the scattering of light caused by the dispersed gel particles 30 in the continuous adhesive 20. The amount or degree of scattering is related to four physical properties: differences in indices of refraction of the various components in the composite, particle size of the gel particles, the weight fraction of the gel particles in the continuous adhesive, and the thickness of the composite.

The difference in the indices of refraction between the pressure sensitive adhesives and the gels of the composite may be as small as 10 percent. In the case of acrylate adhesives and gels of poly (N-vinyl lactams) swollen with glycerol the difference in indices of refraction may be as small as 5 percent, desirably as small as 2 percent and preferably as small as 1 percent to provide a nearly transparent composite.

Further, if the gel particles 30 are larger than the wavelengths of visible light, i.e., greater than 1 micron, then Rayleigh scattering can also be minimized.

Light scattering is also reduced by smaller weight fractions of the gel particles 30 in the adhesive 20, e.g., 30 percent versus 50 percent and the thinner coatings of layer 10 applied to the skin, e.g. 50 microns

versus 100 microns. But these factors must be balanced against the need for strong adhesion and high moisture vapor transmission rate. Nonetheless, even with a weight fraction of gel particles 30 of as much as 95 weight percent dispersed in the adhesive 20 and coatings of the layer 10 of 100 microns thickness applied to the skin, the composites of the present invention can be nearly transparent.

While not intending to be an exhaustive treatment of the embodiments of the present invention, the following examples are illustrative of the scope of the invention which should not be limited thereto or thereby.

15

Example 1

Crosslinked Poly (N-vinylpyrrolidone) Hydrocolloid Bulk Polymerization Using Photochemical Initiation

A solution composed of 0.32 parts 3,3'-ethyldene bis (N-vinyl-2-pyrrolidone), 1.0 parts 2-hydroxy-2-methyl-1-phenyl-1-propanone (serving as the photoinitiator) and 100 parts N-vinyl-2-pyrrolidone were placed in a flat dish at a thickness of 1.3 centimeters and was irradiated through a 0.5 centimeter thick quartz plate with a "Sylvania<sup>R</sup> Sunlamp #052", from GTE Sylvania, Inc., Manchester, N.H., placed at a distance of 40 centimeters for about 20 minutes. The resultant crosslinked poly (N-vinylpyrrolidone) product was ground into a powder of particle size less than 0.25 centimeters using a blender and then thrice both emulsified in water and reprecipitated in acetone to remove residual monomers. The polymer was dried in a vacuum oven at 65°C. The polymer was then again ground into a fine powder using a commercially available grinder, a "Brinkmann Retsch Grinder" from Brinkmann Instruments Company, Westbury, New York. The grinder was used at 20,000 rpm outfitted with a 750 micron grate to provide a

-40-

particle size distribution of 750 microns and smaller, with the majority (by weight percent) of particles between 25 and 200 microns in size. The hard hydrocolloid particles produced are available for swelling into the gel particles.

5

Example 2

Pressure Sensitive Adhesive  
Solution Polymerization

10

This was the pressure sensitive adhesive (PSA) used as the continuous matrix. It did not contain any gel. For this example, it was an isoocetyl acrylate/N-vinyl pyrrolidone copolymer (91/9% weight) dissolved at 25% weight solids in a solvent blend of 15 50/50 heptane/ethyl acetate.

15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 9835 9840 9845 9850 9855 9860 9865 9870 9875 9880 9885 9890 9895 9900 9905 9910 9915 9920 9925 9930 9935 9940 9945 9950 9955 9960 9965 9970 9975 9980 9985 9990 9995 9999

-41-

Example 4

Gel-Adhesive Composite with 10% Gel

To 50 parts of the pressure sensitive adhesive solution described in Example 2 was added 1.39 parts of gel of Example 3 and 2.09 parts of n-heptane and 2.09 parts of ethyl acetate. The mixture was mixed vigorously with a Laboratory Dispersator, Series 2000 model 84, commercially available from Premier Mill Corporation, Reading, Pennsylvania, for several minutes until the gel appeared evenly dispersed. The mixture was allowed to set one minute to allow bubbles to eliminate from the solution and the liquid was coated on a "Poly Slik S-8003" silicone release liner available from H.P. Smith at a thickness of 330 microns (13 mils). The coating was dried 15 minutes at room temperature conditions and then 15 minutes at 79°C. The dried adhesive was then laminated at a pressure of about 3.5 Kg/cm<sup>2</sup> to a segmented block polyester film, prepared from "Hytrel<sup>R</sup> 4056" polyester elastomer available commercially from DuPont de Nemours Company, Wilmington, Delaware. The film thickness was 28 microns.

Example 5

Another Composite-25% Gel

To 50 parts of the adhesive solution described in Example 2 was added 4.17 parts of the gel particles of Example 3, 6.26 parts of n-heptane and 6.26 parts of ethyl acetate. The mixture was prepared, coated and laminated in accordance with Example 4.

-42-

Example 6

Another Composite-50% Gel

To 50 parts of the adhesive solution described  
5 in Example 2 was added 12.50 parts of the gel particles  
of Example 3, 18.75 parts of n-heptane and 18.75 parts of  
ethyl acetate. The mixture was prepared, coated and  
laminated in accordance with Example 4.

10

Example 7

Another Composite-75% Gel

To 30 parts of the adhesive solution described  
in Example 2 was added 22.50 parts of the gel particles  
15 of Example 3, 3.75 parts of n-heptane and 3.75 parts of  
ethyl acetate. The mixture was prepared, coated and  
laminated in accordance with Example 4.

20

25

30

35

The foregoing examples 4-7 illustrate the  
effect that the weight percent of gel, dispersed in an  
acrylic pressure sensitive adhesive, had on moisture  
vapor transmission rates (MVTR) of the composite. The  
results are shown in Table 1. The MVTR for each sample  
of the composite was determined using a variation of a  
ASTM method E96-80. The film was placed adhesive side  
down over the opening of a standard glass vessel half  
filled with deionized water. The MVTR was determined by  
first allowing the sample 24 hours to equilibrate to the  
test conditions of 39°C and 20% ambient relative humidity  
and then measuring the weight loss in the following 24  
hours. The results described in Table 1 demonstrate a  
dramatic increase in the MVTR of the laminate.

To more fully understand the actual improvement  
made to the composite over the use of adhesive alone, the  
MVTR for the composite was mathematically segregated.

The following expression was used for calculating the MVTR of a two layer laminate of polymeric film and the composite.

5            $\frac{1}{\text{MVTR (film)}} + \frac{1}{\text{MVTR (composite)}} = \frac{1}{\text{MVTR (laminate)}}$

The MVTR of the film alone was also determined in order to solve the equation. Since the effect of higher coating weights will reduce the MVTR, the results 10 have been normalized to the same coating weight in order for more meaningful comparisons to be made. These results demonstrate a very dramatic rise in MVTR by the various composites over the MVTR shown for the pressure sensitive adhesive alone.

15

20

25

30

35

5  
10  
15  
20  
25  
30  
35

TABLE I

<u>Example</u>	<u>Weight Fraction Ratio of PSA: Hydrocolloid: Swelling Agent</u>	<u>Coating Weight mg/cm<sup>2</sup></u>	<u>Water Loss in 24.5 hr (g)</u>	<u>Laminate MVTR g/m<sup>2</sup>/24 hr</u>	<u>Composite MVTR g/m<sup>2</sup>/24 hr</u>	<u>Normalized Composite MVTR</u>	<u>% Increase in MVTR</u>
2	100 : 0 : 0	11.1	0.190	367	489	489	—
4	90 : 0.50 : 9.5	9.7	0.240	464	677	586	20
5	75 : 1.25 : 23.75	10.2	0.293	566	918	896	83
6	50 : 2.50 : 47.5	6.7	0.467	903	2329	1412	189
7	25 : 3.75 : 71.25	24.0	0.423	818	1836	3961	710
<u>Film of Hytrel® 4056</u>		—	0	0.763	1475	—	—

The results shown in Table I demonstrate a dramatic improvement in the normalized MVTR of the composites of Examples 4-7 over the MVTR of the pressure sensitive adhesive alone. As the last column demonstrates, in the composite where the pressure sensitive adhesive is an acrylate/N-vinyl-2-pyrrolidone copolymer (IOA/NVP) and the hydrocolloid is poly N-vinyl-2-pyrrolidone (PNVP), the MVTR increased rapidly with increased percentage by weight of the PNVP swollen with glycerol into a gel. Between almost 200 and 700 percent improvement was achieved by incorporating between 50 and 75 weight percent of gel in the composite. Less than 6% of the gel was hydrocolloid, demonstrating significant MVTR with a high loading of swelling agent in the gel: a ratio of hydrocolloid to swelling agent of 1:19 (1.25:23.75).

#### Examples 8-17

##### Determination of Relative Skin Adhesion Using Another Composite Formulation

Consequential to the dramatic improvement in MVTR, it was important to know what change in skin adhesion had occurred at these high gel loadings in the composite and the high weight percent ratio of swelling agent to hydrocolloid in the gel. A central composite design was utilized to assess the influence on skin adhesion of the gel weight fraction in the composite over the range of 0-50% and percent hydrocolloid in the gel over the ratios of 1:20 to 1:1. The hydrocolloid of Example 8 was used in the following formulations, examples 9-17.

-46-

Example 8

Crosslinked PNVP Hydrocolloid

A solution consisting of 0.16 parts of 3,3'-  
5 ethyldene bis (N-vinyl-2-pyrrolidone), 1.0 parts  
2-hydroxy-2-methyl-1-phenyl-1-propanone, (serving as the  
photoinitiator) and 100 parts of N-vinyl-2-pyrrolidone  
was polymerized and processed in the manner described in  
Example 1.

10

Example 9-17

Example formulations 9-17 were prepared by the  
following procedure. The cross-linked poly (N-vinyl  
15 pyrrolidone) samples of Example 8 in the various weights  
shown in Table II were first swollen in a solution of  
glycerol and water in the parts by weight shown in Table  
II to achieve approximately 5% PNVP polymer solids,  
providing a weight ratio of 1:20. This produced a thick  
20 gel paste which was easily dispersible.

The various gel particles of Examples 9-17 were  
sheared with a "Laboratory Dispersator" mixer into a  
mixture of the pressure sensitive adhesive prepared  
according to Example 2.

An additional 20 parts by weight of n-heptane  
25 was then added as the mixture was sheared vigorously for  
between 5 and 10 minutes using a "Laboratory Dispersator"  
mixer. Following shearing, the mixture was allowed to  
stand one minute to eliminate bubbles from the solution  
30 and was coated on the H.P. Smith "Poly Slik S-8003" brand  
release liner. The composite was dried 10 minutes at  
room temperature and oven dried at 93° C for one hour to  
remove the volatile n-heptane and ethyl acetate and the  
water from the gel and adhesive in the composite.

35

TABLE II  
Gel and Composite Formulation (Parts by Weight)

	<u>Example</u>	<u>Glycerol</u>	<u>Deionized Water</u>	<u>Composite</u>		<u>Coating mg/cm<sub>2</sub></u>
				<u>Ex. 8</u>	<u>Ex. 2*</u>	
5	2	0	0	0	100.0	5.2
	9	1.08	15.32	0.82	98.1	4.1
	10	1.68	2.72	0.22	98.1	3.4
	11	3.85	73.15	3.85	92.3	2.5
10	12	5.58	36.82	2.12	92.3	3.4
	13	5.58	36.82	2.12	92.3	3.6
	14	7.31	0.49	0.39	92.3	4.6
	15	8.89	127.31	6.81	84.3	4.3
	16	13.88	22.52	1.82	84.3	6.6
15	17	14.50	95.50	5.50	80.0	4.0

\* The PSA weight is one quarter of the amount in this column because it is a 25% solution of PSA solids.

20 Two coated adhesive samples of each of the above examples were removed from the release liner and were hot laminated at 93°C and 3.5 Kg/cm<sup>2</sup> pressure to two different films, 28 microns thick, prepared from "Hytrel 4056" and "Hytrel 3548" brand polyester elastomers commercially available from DuPont.

25 Skin adhesion of the samples laminated with film prepared from "Hytrel 4056" polyester elastomer was measured initially, after four hours and after 24 hours.

30 The following protocol was used. The backs of six subjects were first wiped clean with a 70:30 solution of isopropanol:water. Once the alcohol had dried, six samples, per formulation, 1.3 centimeters by 10 centimeters, were applied to each subject's back.

35 Two tapes of each formulation were removed per removal time using a 180 degree peel at 30.5 centimeters per minute at T<sub>0</sub> (within ten minutes of application), T<sub>4</sub>

-48-

(after four hours), and  $T_{24}$  (after 24 hours). Then results of both samples for each time interval were averaged and reported as grams per centimeters in Table III.

5           The second skin panel test evaluated skin adhesion to sweaty skin using samples of Examples 2, 9-17 laminated to "Hytrel 3548" film prepared from polyester elastomer. The skin was not prepped with alcohol.

10          Two samples, per formulation, 1.3 centimeters by 10 centimeters were applied, to each of six subjects having dry skin. The subjects road a stationary bicycle for ten minutes in order to begin sweating. Two more samples were applied to the subjects' now wet back. The subjects then road the bike for 20 additional minutes, to 15 continue sweating. Following this time, all of the samples were removed in the same manner at 180 degree peel at 30.5 centimeters per minute. The 180° peel force results were averaged and reported in Table III as applied to dry skin and applied to wet skin. An additional and noteworthy observation was that in none of 20 the samples was there edge lift or, with one exception, any residue left on skin.

25

30

35

35      30      25      20      15      10      5

TABLE III  
SKIN ADHESION

Example	PSA:Hydrocolloid:Swelling Agent	180° Peel Strength				180° Peel Strength			
		T <sub>0</sub> g/cm	T <sub>4</sub> Hours	T <sub>24</sub> Hours	Applied Dry g/cm	Applied Wet g/cm	Applied Dry g/cm	Applied Wet g/cm	
2	100 : 0 : 0	62	103	114	53	45			
9	92.8 : 3.1 : 4.1	52	87	102	54	43			
10	92.8 : 0.8 : 6.4	52	87	99	46	40			
11	75 : 12.5 : 12.5	49	83	109	47	42			
12	75 : 6.9 : 18.1	47	88	98	45	34			
13	75 : 6.9 : 18.1	50	85	100	43	35			
14	75 : 1.25 : 23.75	51	91	94	47	37			
15	57.3 : 18.5 : 24.2	42	82	80	40	34			
16	57.3 : 5 : 37.7	63	96	52*	56	41			
17	50 : 13.75 : 35.25	49	89	84	49	41			

\* Trace of glycerol residue

-50-

It is apparent that the incorporation of 25% weight fraction of gel to the composite (Examples 11-14) had only a slight impact on skin adhesion of the composite. Even levels of 50% weight fraction of gel (Example 17) resulted in little change to the skin adhesiveness of the composite of various weight fractions. Skin adhesiveness did not vary considerably whether applied dry, applied wet, or maintained on the skin for a few minutes, four hours, or one day.

Equally surprising was that residuing and lifting was not a problem, except for Example 16 which left a trace of glycerol residue, and even then only after 24 hours of continuous use.

These results confirmed that this composite truly incorporated the MVTR benefits of gel polymers with almost no degradation in adhesive performance of acrylate adhesives.

#### Examples 18-21

#### Incorporation Of Antimicrobial Agents Into The Composites

The purpose of the following examples 18-21, was to demonstrate the dramatic increase in antimicrobial activity even at relatively low loadings of gel, 25% by weight fraction of gel in the gel-adhesive composite, (i.e., excluding the weight of the antimicrobial agent until the weight fractions of gel-adhesive composite were determined.)

Controls were used for comparing the performance of the antimicrobial containing composite. These controls included "Ioban<sup>TM</sup> 2" brand antimicrobial film, the adhesive thereof containing 2% iodine; "Opsite CH<sup>TM</sup>" brand incise drape, the adhesive thereof containing 5% chlorhexidine acetate; and "Steri-Drape<sup>TM</sup> 2" incise drape, the adhesive thereof not containing an antimicrobial agent. "Ioban 2<sup>TM</sup>" and "Steri-Drape<sup>TM</sup> 2"

-51-

brand incise drape are both commercially available from 3M Company, St. Paul, Minnesota. "Opsite CH<sup>TM</sup>" brand incise drape is commercially available from Smith and Nephew Medical Limited, Hull, HU32BN England.

5

Examples 18-21

These examples utilized the cross-linked poly (N-vinyl pyrrolidone) of Example 8 which was first swollen by a solution containing water, glycerol and antimicrobial (e.g. iodine and sodium iodide or chlorhexidine gluconate solution) in the parts by weight shown in Table IV.

The swollen gel paste was then dispersed into the acrylic adhesive solution of Example 2 with a "Laboratory Dispersator" mixer, vigorously for between 5 and 10 minutes until the gel was fully mixed. An additional 20 parts (wt.) of n-heptane is added to assist in the dispersion process. The solution was sheared for several minutes or until uniform and free of agglomerates. The mixture was allowed to stand for one minute, to eliminate bubbles prior to coating on a H.P. Smith "Poly Slik S-8003" brand release liner. The composite was dried 10 minutes at room temperature and then oven dried at 80°C for one hour. The coated adhesive samples were removed from the release liner and hot laminated at 93°C at 3.5 Kg/cm<sup>2</sup> pressure to 28 microns (1.1 mil) thick film prepared from "Hytrel<sup>R</sup> 3548" brand elastomer.

30

-52-

TABLE IV  
Gel and Composite Formulation (Parts by Weight)

			20%				
			PNVP			CHg*	PSA
			Distilled of			in	of
Example	Glycerol	Water	Ex. 8	Iodine	NaI	Water	Ex. 2**
18	5.58	36.82	2.12	0.61	0.77	---	92.30
19	13.88	22.52	1.82	0.78	0.93	---	84.30
10 20	5.58	30.67	2.12	---	---	7.65	84.90
21	13.88	15.07	1.82	---	---	9.25	77.56

\* 20% chlorhexidine gluconate in water.

\*\* 25% weight percent of PSA solids in grams of PSA  
solution

Antimicrobial activity In Vitro testing results for the controls and the laminated composites of Examples 18-21 are presented in Table V below. The Ulrich procedure was used for the test, according to the procedure identified in Infection in Surgery, August 1984, 569-574, as modified below.

Ulrich Procedure For Determining  
Antibacterial Activity  
Of Transparent Dressings

Specimens were handled aseptically on a laminar flow clean bench which was disinfected with isopropanol prior to use. The laminated composites were each cut into one inch squares. Liner was removed with the aid of sterile forceps and the film backing placed coating-up on a raised surface in the bottom of a moist chamber.

Just prior to application, *Streptococcus faecalis* was grown on m-enterococcus agar. The suspension was adjusted turbidimetrically to contain at least  $10^8$  bacteria/ml and a viable count was made by the

-53-

pour-plate method. A micropipette was employed to deposit and distribute 0.05 ml of this suspension on the adhesive surface; the contents were first spotted over the entire surface and then spread evenly with the  
5 pipette tip.

At time intervals of 10, 30, 60, and 90 minutes the seeded squares were removed and separately placed in blenders containing 100 ml of 6.25 fold strength "Difco" brand neutralizing buffer commercially available from  
10 Baxter Health Care Corp. This concentration is not inhibitory for most bacteria and negates transfer of both antimicrobials to the rinsing fluid. The samples were essentially macerated by five minutes agitation at full speed. An aliquot of rinsing fluid was decanted from the  
15 blender cup and exponentially diluted in sterile physiological saline. The following dilutions were plated in m-enterococcus agar to provide viable counts: undiluted,  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ ; an initial dilution of  $10^{-2}$  was imposed on these counts by the  
20 rinsing fluid. Plates were incubated overnight at 35°C and enumerated with the Biotran II automatic colony counter.

The  $\log_{10}$  reduction in bacterial numbers was determined by the numerical difference between the  
25 inoculum and recovery values. Duplicate platings on duplicate specimens were averaged to obtain final numbers.

30

35

-54-

30  
25  
20  
15  
10  
5

TABLE V  
IN VITRO ANTIMICROBIAL EFFICACY  
Log Reduction (*S. faecalis*)

<u>Example</u>	<u>Weight Fraction Ratio</u> <u>PSA:Hydrocolloid:Swelling Agent</u>	<u>Antimicrobial</u>	Ulrich Procedure				<u>Antimicrobial Activity</u>
			<u>min</u>	<u>min</u>	<u>min</u>	<u>min</u>	
18	75 : 6.88 : 18.12	2% Iodine	1	5	—*	4	
19	57.3 : 5 : 37.7	2% Iodine	Ni1	3	—*	6	
20	73.4 : 7.3 : 19.3	5% Chlorhexidine	3	5	—*	5	
21	55.25 : 5.2 : 39.55	5% Chlorhexidine	2	2	—*	6	
"Ioban™ 2" Antimicrobial Film	—	2% Iodine	Ni1	3	5	5	
"OPSITE™ CH" Drape	—	5% Chlorhexidine	0	—*	0	—*	
"STERI-DRAPE™ 2" Drape	—	(NO ANTIMICROBIAL)	0	0	—*	0	

\*Not measured

-55-

The results indicate that chlorhexidine did not appear to be active in the "Opsite<sup>TM</sup> CH" incise drape control but was very active in the composite of Example 20 and 21. Iodine was very active from the "Ioban<sup>TM</sup> 2" antimicrobial film control, but the composite of Examples 18 and 19 showed comparable iodine activity.

Examples 22-33

The next Examples 22-33 demonstrated the broad flexibility in formulating these gel-adhesive composites. Table VI shows the formulations of the composites in parts by weight having the antimicrobial agent therein.

The procedure for preparing these examples was the same as that outlined in Examples 18-21, except that the percent of PSA solids was slightly higher resulting in recalculation of the weight fraction of the PSA in the final composite.

20  
TABLE VI  
Gel and Composite Formulations (Parts by Weight)

	<u>Example</u>	<u>Glycerol</u>	<u>Distilled Water</u>	PNVP		PSA (27.6% solids) of <u>Example 2</u>
				<u>Ex. 8</u>	<u>20% CHg* in water</u>	
25	22	0.85	14.55	0.77	3.7	58.38
	23	2.15	14.65	0.84	3.9	57.02
	24	1.41	29.99	1.57	3.9	66.95
	25	5.69	22.71	1.42	4.6	52.88
30	26	3.74	63.89	3.38	4.6	52.88
	27	3.74	63.89	3.38	4.6	52.88
	28	3.74	63.86	3.38	4.6	52.88
	29	3.74	63.86	3.38	4.6	52.88
	30	1.78	105.02	5.34	4.6	52.88
35	31	9.40	63.93	3.67	5.6	46.93
	32	4.32	170.71	8.75	5.6	46.93
	33	8.59	146.81	7.77	6.1	43.64

\* 20% chlorhexidine gluconate in water.

-56-

Table VII demonstrated that even as the weight fraction of the gel was varied from 10-60%, acceptable adhesion and in most cases superior antimicrobial gel-adhesive composites were possible.

5

10

15

20

25

30

35

**TABLE VII**  
**In Vitro Test vs. strep. faecalis (ATCC 10741)**  
**And Skin Adhesion**

Example	Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent	180° Peel Strength			Ulrich Procedure		
		T <sub>0</sub> Hour	T <sub>1</sub> Hour	T <sub>6</sub> Hour	g/cm	g/cm	6 min
22	90.9 : 4.3 : 4.8	45.9	81.1	97.1	1.0	1.0	5.0
23	84 : 4.5 : 11.5	46.1	78.3	82.5	2.0	2.0	5.0
24	86.1 : 7.3 : 9.0	43.9	74.9	82.8	2.0	2.0	5.0
25	67.3 : 6.5 : 26.2	51.6	84.9	101.0	2.0	2.0	4.0
26	67.2 : 15.6 : 17.2	45.6	66.1	79.1	2.0	2.0	5.0
27	67.2 : 15.6 : 17.2	45.4	66.2	79.2	2.0	2.0	5.0
28	67.2 : 15.6 : 17.2	45.4	66.8	79.8	2.0	2.0	5.0
29	67.2 : 15.6 : 17.2	45.4	66.1	78.7	2.0	2.0	5.0
30	67.2 : 24.6 : 8.2	20.8	36.1	61.8	2.0	2.0	5.0
31	49.8 : 14.1 : 36.1	42.8	78.0	86.6	3.0	3.0	5.0
32	49.8 : 33.6 : 16.6	14.6	25.8	43.9	1.0	1.0	5.0
33	42.4 : 27.4 : 30.2	31.9	56.9	73.2	2.0	2.0	3.0
"Ioban™ 2"	100 : 0 : 0	54.8	71.1	88.6	Nil	Nil	<1.0

As can be seen by referring to Table VII, there was no significant variance among the various gel-adhesive composites as to the antimicrobial activity. Indeed throughout a broad range of weight fractions of the gel, the antimicrobial activity was consistently excellent and compares favorably with "Ioban<sup>TM</sup> 2" brand antimicrobial film, which is an iodine antimicrobial incise drape without gel therein.

10

Examples 34-44

## Necessity Of Hydrocolloid And Non-Volatile Swelling Agent

15

20

25

30

35

The following examples illustrate the importance of swelling the hydrocolloid with a non-volatile swelling agent. Example formulations 35, 36, 39, and 40 were prepared by the same procedure as outlined for Examples 9-17, according to the formulations identified in Table VIII, with the exception that the coatings were dried 30 min. at 22°C followed by oven drying for 20 min. at 80°C. Example formulations 37, 38, 41, and 42 were prepared according to the same procedure as Examples 35, 36, 39, and 40, except that in the formulation of the hydrocolloid, no crosslinking agent was used. Example 34 was a repeat example of pressure sensitive adhesive, and Example 44 was a comparison example mixing the swelling agent without hydrocolloid into the adhesive.

-59-

35  
30  
25  
20  
15  
10  
5

TABLE VIII  
Gel and Composite Formulations (Parts by Weight)

<u>Example</u>	<u>Glycerol</u>	<u>Deionized Water</u>	<u>Crosslinked Hydrocolloid of Example 8</u>	<u>Linear PVNP (360,000 M.W.)</u>	<u>PSA (28% Solids) of Example 2</u>	<u>Heptane</u>
	34	0	0	0	50.0	0
35	7.0	30.5	3.0	0	107.1	20.3
36	14.0	61.0	6.0	0	71.4	21.4
37	7.0	5.0	0	3.0	107.1	29.5
38	14.0	10.0	0	6.0	71.4	35.5
39	0	0	5.0	0	53.6	21.1
40	0	0	5.0	0	35.7	19.3
41	0	0	0	5.0	53.6	10.8
42	0	0	0	5.0	35.7	19.3
43	10.0	0	0	0	107.1	22.2
44	20.0	0	0	0	71.4	19.7

-60-

The dried adhesives were hot laminated at 93°C to 28 micron (1.1 mil) thick film prepared from "Hytrel® 4056" brand elastomer film. These samples were evaluated for T-Peel adhesion to 20 micron thick low density polyethylene film. Moisture vapor transmission rates were also determined in the same manner as described in Examples 4-7. The results are reported in Table IX below.

T-peel tests were performed on each sample by using a variation of ASTM D 1876 on an Instron Model 1122 stress analyzer. The samples were cut to 2.54 cm by 10.2 cm, removed from the release liner, and laminated with a 2.25 Kg roller onto 20 micron thick low density polyethylene (LDPE) film. Six samples for each test were made and tested, the averaged values were reported. The samples were tested under two sets of conditions. The first set of conditions was to age the samples 10 days at room temperature (22°C) prior to testing. The second set of conditions was to age the samples at 50% relative humidity and 21°C for 6 days. The jaw separation speed on the Instron Model 1122 stress analyzer was 25.4 cm/min.

25

30

35

35      30      25      20      15      10      5

TABLE IX

<u>Example</u>	<u>Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent</u>	<u>T-Peel Adhesion (g/cm)</u>			<u>Laminate MVTR g/m<sup>2</sup>/24 hours</u>
		<u>LDPE</u>	<u>22°C</u>	<u>21°C/50R.H.</u>	
34	100 : 0 : 0	68	59	408	
35	75 : 7.5 : 17.5	68	63	619	
36	50 : 15 : 35	80	114	797	
37	75 : 7.5 : 17.5	54	52	856	
38	50 : 15 : 35	68	79	1066	
39	75 : 25 : 0	66	61	800	
40	66.7 : 33.3 : 0	23	20	N/A*	
41	75 : 25 : 0	45	38	988	
42	66.7 : 33.3 : 0	11	25	N/A	
43	75 : 0 : 25	61**	59**	533	
44	50 : 0 : 50	66**	70**	1001	
Film of "Hytrel® 4056" brand polyester elastomer —					
		—	—	—	1376

\* Samples without defects to the adhesive could not be made.

\*\* Surface of sample showed glycerol residual which bloomed to the surface.

Examples 35 and 36 utilized crosslinked PNVP hydrocolloid while Examples 37 and 38 utilized uncrosslinked PNVP hydrocolloid. By comparison, Examples 35 and 38 utilized non-volatile glycerol while Examples 39-42 utilized no swelling agent, with a further comparison of crosslinked hydrocolloids in Examples 39 and 40 and uncrosslinked hydrocolloids in Examples 41 and 42. Finally, Examples 43 and 44 used no hydrocolloid with unacceptable results footnoted.

The use of a swelling agent in the gel (Examples 35-38) allowed the composite to substantially retain or even increase the adhesiveness of the pressure sensitive adhesive. For example, the T-Peel adhesive strength on LDPE at 22°C of Example 36 is greater than the IOA/NVP PSA of Example 34, the unswollen stoma-type adhesives of Example 39 and 40 using crosslinked PNVP hydrocolloid, and the unswollen stoma-type adhesives of Examples 41 and 42 using uncrosslinked PNVP hydrocolloid. A comparable favorable result was obtained after aging in humid conditions. And MVTR was nearly twice the amount as that of the PSA alone of Example 34. The comparative results for Examples 35, 37 and 38 were not as dramatic. But generally the adhesive strength of these Examples were comparable to the pressure sensitive adhesive of Example 34 and the MVTR is 150-175% percent greater.

Table IX also shows the comparison of crosslinked PNVP vs. uncrosslinked PNVP both swollen into a gel and unswollen as a hydrocolloidal material in a stoma-type adhesive. The T-Peel strength on LDPE results were greater for crosslinked PNVP than the uncrosslinked PNVP, both in dry and for humid conditions. Thus, crosslinked PNVP is preferred to uncrosslinked PNVP. Examination of the MVTR results of crosslinked and uncrosslinked PNVP showed that uncrosslinked PNVP and crosslinked PNVP are acceptable and superior to the adhesive of Example 34.

-63-

Table IX also shows the unacceptable results of the attempt to formulate a composite without the presence of hydrocolloid. Examples 43-44 showed the effects of incompatible blooming of the glycerol to the surface of the composition, an unacceptable condition. Further, these adhesion values shown for Examples 43-44 will fall dramatically as the composite ages and more glycerol blooms to the surface.

10

Examples 45-53

Composites Prepared From A  
Latex Of Hydrophobic PSA In An Aqueous Solution

15

These examples utilized a latex base PSA, such that the hydrocolloid was placed in the continuous water phase. The examples demonstrated the superior MVTR performance of composite prepared by this technique and the importance of the swelling agent to the composite.

20

The formulations were prepared by first swelling the PNVP in the glycerol and water. The swollen gel was then blended into a PSA latex ("Rhoplex<sup>®</sup> E-1960D 53.0% N.V.", available from Rohm & Haas Co. Philadelphia, PA) by a "Laboratory Dispersator" mixer from Premier Mill Corporation. The final non-volatiles were calculated and a coating thickness was estimated to produce 80 microns of dried composite. The samples were coated on release liner and dried at 22°C for 30 min followed by 20 min. at 80°C. The dried composite was hot laminated at 93°C to 28 micron thick film prepared from "Hytrel<sup>®</sup> 4056" brand polyester elastomer. Specific formulations in the latex are identified in Table X, and T-Peel strength and MVTR results, measured in the same manner as for Examples 34-44 are reported in Table XI.

35

5  
10  
15  
20  
25  
30  
35

TABLE X  
Gel and Composite Formulations (Parts By Weight)

<u>Example</u>	<u>Glycerol</u>	<u>Deionized Water</u>	<u>PNVP of Example 8</u>	<u>PNVP (360,000 M.W.)</u>	<u>53% Solids "Rhoplex<sup>R</sup> E-1960D" Latex</u>
45	0	0	0	0	50.0
46	7.0	45.1	3.0	0	56.6
47	14.0	58.3	6.0	0	37.7
48	7.0	33.4	0	3.0	56.6
49	14.0	42.3	0	6.0	37.7
50	0	35.1	2.5	0	14.2
51	0	48.4	5.0	0	9.4
52	0	12.0	0	5.0	28.3
53	0	18.0	0	5.0	9.4
Film of "Hytrel <sup>R</sup> 4056" brand polyester elastomer					
<u>—</u>					

5  
10  
15  
20  
25  
30  
35

TABLE XI

<u>Example</u>	<u>Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent</u>	<u>T-Peel Adhesion (g/cm)</u>			<u>Laminate MVTR q/m<sup>2</sup>/24 hours</u>
		<u>LDPE</u>	<u>22°C</u>	<u>21°C/50R.H.</u>	
45	100 : 0 : 0	66	95	619	
46	75 : 7.5 : 17.5	75	98	948	
47	50 : 15 : 35	127	198	1442	
48	75 : 7.5 : 17.5	39	139	928	
49	50 : 15 : 35	80	93	1350	
50	75 : 25 : 0	13	4	1178	
51	50 : 50 : 0	0	0	1211	
52	75 : 25 : 0	0	0	1205	
53	50 : 50 : 0	0	0	1198	
Film of "Hytrel <sup>R</sup>					
4056" brand					
Polyester Elastomer					
					1376

Examples 46 and 47 demonstrated the use of swollen gel of crosslinked PNVP. Examples 48 and 49 demonstrated the use of swollen gel of uncrosslinked PNVP. Examples 50 and 51 demonstrated the use of gel of crosslinked PNVP temporarily swollen by water. Examples 52 and 53 demonstrated the use of gel of uncrosslinked PNVP temporarily swollen by water.

Again, a comparison of the T-Peel strength on LDPE of the various examples with LDPE aged in dry and wet conditions demonstrated the superior performance of the composites prepared using a non-volatile swelling agent and a crosslinked PNVP hydrocolloid, i.e., Examples 46 and 47. Of the compositions of Examples 50-53 without the non-volatile swelling agent, only the composition of Example 50 has any T-Peel adhesion at all, which amount was vastly inferior to the results for any of the compositions of Examples 46-49.

As shown in Table XI, excellent MVTR was provided by the compositions of Examples 46-49, between 1.5 and 2.0 times the MVTR provided by latex-produced PSA of Example 45. While other Examples also had a high MVTR compared with the latex-produced PSA of Example 45, none of them also provided higher T-Peel adhesive strengths than the composite of Example 47.

Data in Table XI also demonstrated by comparison to the data of Table IX that the T-Peel strength of the preferred composites were not adversely affected by the method of preparation of the composite. Whether dispersed into a continuous hydrophobic phase, the results of which are reported in Table IX, or mixed into a hydrophilic latex, the results of which are reported in Table XI, the composites of the present invention provided excellent adhesive strength and high moisture vapor transmission rates.

-67-

Examples 54-59

Gel Particle Size Variations On The Composites

The influence of particle size on adhesion and MVTR was studied. The PNVP particles were prepared by grinding the hydrocolloid polymer of Example 8 through a "Retsch Brinkman" grinder at 20,000 rpm and with a 3/4 mm grate. The particles were then sized through several wire meshes to provide 3 samples ranging from 25-106 microns, 106-212 microns and 300-600 microns. Due to the very fragile nature of the swollen gels during processing, great care was taken to use minimal shear in blending them into the adhesive latex. With this exception, the Examples of 54-59 were prepared in the same manner as for Examples 45-53. Table XII reports the formulations and Table XIII reports the T-Peel adhesive strength and MVTR of each composite of the Examples, as measured in the same manner as that for Examples 35-44.

20

25

30

35

30      25      20      15      10      5

TABLE XII  
Formulations of Gel and Composite (Parts by Weight)

<u>Example</u>	<u>Particle Size</u>		<u>Glycerol</u>	<u>Deionized Water</u>	<u>PNVP of Ex. 8 (sized)</u>	<u>53% Solids "Rhoplex® E-1960D" Latex</u>
	<u>Range of PNVP of Ex. 8</u>	<u>Range of PNVP of Ex. 8</u>				
54	300-600 microns	7.0	53.0	3.0		56.6
55	300-600 microns	14.0	76.0	6.0		37.7
56	106-212 microns	7.0	43.0	3.0		56.6
57	106-212 microns	14.0	76.0	6.0		37.7
58	25-106 microns	7.0	43.0	3.0		56.6
59	25-106 microns	7.0	38.0	3.0		18.9

5  
10  
15  
20  
25  
30  
35

TABLE XIII

<u>Example</u>	<u>Dried Hydrocolloid Particle Size</u>	<u>Weight Fraction Ratio of PSA:Hydrocolloid:Swelling Agent</u>	<u>T-Peel (g/cm)</u>		<u>Laminate MVTR q/m<sup>2</sup>/24 hour</u>
			<u>LDPE</u>	<u>22°C</u>	
54	300-600 microns	75 : 7.5 : 17.5	148	152	889
55	300-600 microns	50 : 15 : 35	125	130	1067
56	106-212 microns	75 : 7.5 : 17.5	291	270	790
57	106-212 microns	50 : 15 : 35	168	148	1106
58	25-106 microns	75 : 7.5 : 17.5	248	273	856
59	25-106 microns	50 : 15 : 35	164	150	1310
45	No Hydrocolloid	100 : 0 : 0	66	95	619
Film of "Hytrel®/4056" brand polyester elastomer			0	—	1376

-70-

The results as reported in Table XIII did not demonstrate a definite particle size performance relationship to adhesion. At the 50:15:35 weight fraction ratio (Examples 55, 57, and 59) MVTR increased as the particle size decreased from 300-600 microns to 5 25-106 microns. However, for composites with less gel dispersed in the adhesive matrix (Examples 54, 56, and 58), even at the same ratio of hydrocolloid to swelling agent, there was no trend between particle size and MVTR.

10

Examples 60-64

Other Hydrocolloids In The Gel-Adhesive Composites

15

The previous examples have all focused on linear or crosslinked poly (N-vinyl pyrrolidone) hydrocolloids swollen with a non-volatile swelling agent. The following examples incorporate two variations in the scope of the invention, a change in the hydrocolloid and a change in the continuous pressure sensitive adhesive matrix.

20

Example 60

Pressure Sensitive Adhesive

25

This example described a pressure sensitive adhesive blend used as the continuous matrix. The adhesive was composed of 50.0 parts "Krayton<sup>R</sup> 1111" brand styrene-isoprene block copolymer from Shell Chem. Co., Houston, Texas and 70.0 parts "Wingtac<sup>R</sup> 95" brand polyterpene resin from Goodyear Tire and Rubber, Akron, 30 Ohio dissolved in 360.0 parts of toluene. The hydrophobic adhesive blend was dissolved in a solvent which phase separated from water.

35

-71-

Example 61  
Guar Gum Hydrocolloid

To 0.9 parts of guar gum ("Uniguar<sup>R</sup> 150" brand  
5 guar gum manufactured by Hi-Tek polymers, Clifton, NJ) was added 2.1 parts glycerol. The guar gum solution was heated for 2 hours at 65°C to enhance the absorbance of glycerol. The swollen gel was mixed vigorously with a "Laboratory Dispersator" mixer with 36.0 parts of Example 10 60, until the gel appeared evenly dispersed. The mixture was allowed to stand for one minute for bubbles to escape. The composite was coated on release liner at a thickness of 0.38 mm. The composite was dried 30 min. at 22°C and 15 min. at 88°C.

15 The dried composite was then hot laminated at 93°C to 28 microns thick film prepared from "Hytrel<sup>R</sup> 4056" brand elastomer.

Example 62  
Xanthan Gum Hydrocolloid

To 0.9 parts of Xanthan Gum ("Keltrol<sup>R</sup>" brand,  
20 manufactured by Merck and Co., Inc. San Diego, CA) was added 2.1 parts glycerol and the mixture heated for 2 hours at 65°C to allow the glycerol to swell the xanthan 25 gum. The swollen gel was mixed vigorously as in Example 61 with 36.0 parts of Example 60 until the gel appeared evenly dispersed. The coating, drying and laminating followed the steps of Example 61.

30  
Example 63  
Hydroxypropyl Methyl Cellulose

To 0.9 parts of Hydroxypropyl Methyl Cellulose (HPMC) ("Methocel<sup>R</sup> J75MS" brand HPMC, manufactured by Dow 35 Chemical, Midland, MI) was added 2.1 parts glycerol and 0.53 parts deionized water and the mixture was heated at

-72-

65°C for 2 hours to allow the glycerol to swell the HPMC. The mixture was mixed with 36.0 parts of the adhesive of Example 60 vigorously as in Example 61 until the gel appeared evenly dispersed. The coating, drying, and laminating followed the steps of Example 61.

5

Example 64

Alginat

10 To 2.0 parts sodium Alginat ("Kelgin® MV" brand, alginat manufactured by Merck & Co, Inc., San Diego, CA) were added 2.5 parts  $\text{CaSO}_4$ , 0.8 parts  $\text{Na}_3\text{PO}_4$ , 20.0 parts glycerol and 60.0 parts deionized water. The sample was mixed and allowed to stand for several hours to form a firm gel. The gel was placed in a "Waring" 700 Model #31BL46 brand blender and ground at the uniform speed of the blender to produce small particle sized gels of less than about 200 microns. 67.3 parts of the gel particles were then mixed with 80.0 parts of the adhesive of Example 60 vigorously as in Example 61 until the gel appeared evenly dispersed. The coating, drying and laminating followed the steps of Example 61.

15

20

25

T-Peel and MVTR results for the composites of Examples 60-64 are reported in Table XIV.

30

35

5  
10  
15  
20  
25  
30  
35

TABLE XIV

Example	Hydrocolloid	Weight Fraction Ratio of PSA:Hydrocolloid: Swelling Agent	T-Peel (g/cm)		Laminate MVTR	$\frac{g/cm^2}{24\text{ hr}}$	Dried Coating wt. $mg/cm^2$	Normalized to $6.64\text{ mg/cm}^2$ Coating wt.
			LDPE	LDPE				
60	None	100 : 0 : 0	200	232	158	3.33	3.33	84
61	Guar Gum	75 : 7.5 : 17.5	284	307	336	5.79	5.79	328
62	Xanthan Gum	75 : 7.5 : 17.5	166	105	356	7.64	7.64	393
63	HPMC	75 : 7.5 : 17.5	182	245	138	7.76	7.76	159
64	Alginate	53.5 : 4.3 : 42.2	218	279	375	9.87	9.87	492

Table XIV demonstrated that the T-Peel adhesive strength of a variety of hydrocolloids was in the range of acceptable PSA T-Peel strengths in both dry and wet conditions. But the MVTR of the composites of Examples 5 61-64 were significantly greater than the PSA of Example 60. Thus, a variety of hydrocolloids were acceptable in the gel-adhesive composite of the present invention.

Examples 65-71

10 Other Gel-Adhesive Composites Having Large Weight Fractions Of Gel Therein

The following examples demonstrated the amount of swollen gel which can be dispersed into the pressure sensitive adhesive matrix before the adhesion of the 15 resulting composite suffers. Example formulations 65-70 were prepared by the same procedures outlined in examples 34-44 with the exception that the composites were air dried 15 min at 22°C and oven dried at 100°C for 2 hours. 20 Example 71 was mixed and pressed to a thickness of 0.22 mm and laminated to 28 micron thick film prepared from "Hytrel® 4056" brand polyester elastomer. T-Peel Adhesion to LDPE was measured under the same conditions as that used for Examples 34-44, in dry humidity at 22°C. 25 Table XV identifies the formulations and Table XVI reports the results.

30  
25  
20  
15  
10  
5

TABLE XV  
Gel and Composite Formulations (Parts by Weight)

<u>Example</u>	<u>Glycerol</u>	<u>Water</u>	<u>PNVP of Ex. 1</u>	<u>PSA (25.0% solids) of Ex. 2</u>	<u>n-Heptane</u>	<u>Dried Coating at mg/cm<sup>2</sup></u>
	Deionized					
65	0	0		100.00	0	5.68
66	.75	2.50	.25	76.00	10.0	5.17
67	9.00	30.00	3.00	32.00	20.0	5.55
68	10.50	35.00	3.50	24.00	20.0	5.43
69	11.25	37.50	3.75	20.00	20.0	4.71
70	12.00	40.00	4.00	16.00	20.0	5.30
71	9.00	0	3.0	0	0	25

TABLE XVI

5	Example	Weight Fraction Ratio of PSA:Hydrocolloid:	T-Peel Adhesion
		Swelling Agent	(g/cm) on LDPE
	65	100 : 0 : 00	66
	66	95 : 1.25 : 3.75	63
	67	40 : 15 : 45	107
10	68	30 : 17.5 : 52.5	76
	69	25 : 18.75 : 56.25	68
	70	20 : 20 : 60	49
	71	0 : 75 : 25	8.5

15 As the percentage of PSA decreased, the T-Peel adhesion of the composite against LDPE rose and fell. Except for Example 65 containing no gel, the hydrocolloid:swelling agent weight fraction ratio for the other Examples 66-71 was a constant weight fraction ratio of 1:3. When considering only the results of T-Peel adhesion, the variation of only the weight fractions of the gel to the PSA demonstrated that a possible range of gel weight fractions was from about just greater than 0, about 5, (Example 66) to about 75 percent (Example 69), i.e., the weight fraction sum of the hydrocolloid and the swelling agent. At ratios of PSA/gels ranging from about 40:60 to about 25:75, (Examples 67-69), where the ratio of the hydrocolloid was constant at 1:3, the T-Peel adhesive strength in the gel-adhesive composite even exceeded the T-Peel adhesive strength of the PSA alone.

Examples 72-78

## Other Gel Weight Fraction Ratio Limits

35 Example 30 demonstrated a useful formulation containing PNVP hydrocolloid to glycerol swelling agent ratio of 3:1 (24.6:8.2). The skin adhesion results for

Example 30 showed less peel adhesion than other compositions such as Examples 25-29 having the same weight fraction of gel in the composite but having a greater weight fraction of swelling agent in the gel.

5       The following examples demonstrated the acceptable and preferred ranges of the weight fraction ratios of hydrocolloid to swelling agent. T-peel adhesion results measured in the same manner as for Examples 34-44 to low density polyethylene (LDPE) are reported in Table XVIII below.

10      LDPE is not a perfect skin substitute for adhesion testing but does represent the general trends in adhesion. At a very high hydrocolloid/swelling agent weight fraction ratio, such as 42.5:7.5 or 5.7:1 (Example 15 78), the adhesive strength was comparable to unswollen hydrocolloids, i.e., see Example 40. Example formulations 72-78 were prepared by the same procedure outlined in examples 65-70 and are identified in Table XVII. T-Peel adhesive strength was measured in the same manner as for Examples 65-71.

20

TABLE XVII  
Gel and Composite Formulations (Parts by Weight)

	Example	Glycerol	Water	PSA			Coating wt mg/cm <sup>2</sup>
				Deion- ized	PNVP of solids)	(25.0%	
30	72	7.13	3.80	.38	30.0	10.0	5.36
	73	6.75	7.50	.75	30.0	10.0	4.65
	74	6.00	15.00	1.50	30.0	10.0	4.97
	75	4.50	30.00	3.00	30.0	10.0	5.55
	76	2.00	30.00	3.00	20.0	10.0	5.62
	77	1.25	37.50	3.75	20.0	10.0	6.07
35	78	0.75	42.50	4.25	20.0	10.0	6.26

TABLE XVIII

5	<u>Example</u>	<u>Weight Fraction Ratio of PSA:Hydrocolloid: Swelling Agent</u>	<u>T-Peel Adhesion (g/cm) on LDPE</u>
	70	100 : 0 : 0	66
10	72	50 : 2.5 : 47.5	99
	73	50 : 5 : 45	80
15	74	50 : 10 : 40	108
	75	50 : 20 : 30	68
20	76	50 : 30 : 20	28
	77	50 : 37.5 : 12.5	29
25	78	50 : 42.5 : 7.5	25
	40	66.7 : 33.3 : 0	23

As illustrated in Table XVIII, the T-Peel strength also rose and fell throughout increasing weight fraction ratios of hydrocolloids to swelling agents. Based on the variation of such weight fraction ratios and a constant weight fraction of the swollen gel in the composite, a desirable range extended from about 1.5:1 to about 1:19 (Examples 72-76) with a preferable range for the better balance of properties being from about 1:1.5 to about 1:19 (Examples 72-75).

Examples 79-86Determination Of Acceptable Shear Modulus Of The Gel

The following examples 79-86 quantified the shear modulus range for the gels in the gel-adhesive composites of the present invention. The samples were prepared by mixing powdered poly (N-vinyl pyrrolidone) of example 8 with varying amounts of glycerol. The samples were allowed 24 hours to completely absorb the glycerol, followed by hydraulically pressing the samples between

release liners to a thickness of 1 mm. The resultant gel films were cut to 50 mm diameter circles and tested between 50 mm diameter parallel plates at 22°C on a "Rheometrics Mechanical Spectrometer", Model 605 manufactured by Rheometrics Inc. 1 Possumtown Road, Piscataway, NJ. These details and ASTM D 4065-82 describe the technique used. The Shear Modulus for each samples is reported Table XIX below in dynes/cm<sup>2</sup> at 1 and 5.6 Rad/sec.

10

TABLE XIX  
Gel and Composite Formulations (Parts by Weight)  
and Shear Modulus Results

	<u>Example</u>	<u>PNVP</u>	<u>Weight %</u>	<u>Weight %</u>	<u>Shear Modulus</u>	
			Example 8	Glycerol	<u>1 Rad/Sec.</u>	<u>5.6 Rad/Sec.</u>
	79	5		95	2.95	5.13
	80	10		90	7.20	10.32
20	81	20		80	16.94	26.24
	82	30		70	25.22	42.24
	83	40		60	41.17	74.19
	84	50		50	153.5	179.7
	85	60		40	999.4	2,068
25	86	75		25	6,171	6,423

Examples 30 and 77 having PNVP as the hydrocolloid showed useful formulations containing PNVP hydrocolloid/swelling agent ratios up to 3:1. Since the shear modulus of the gel will vary with the type of hydrocolloid (e.g. PNVP, alginates, cellulosics) and the choice of non-volatile swelling agent, examples 79-86 were important in defining a desired upper modulus. An upper modulus is desired to assure that the gel particles are soft and pliable in the composites.

-80-

There does not appear to be a lower modulus limit; rather there must be at least a minimal amount of hydrocolloid present to prevent the swelling agent from migrating or blooming to the surface of the composite and thereby degrading the adhesive properties thereof. An example of this incompatible blooming was shown by examples 44-45 where no hydrocolloid was present.

The desired upper shear modulus limit for the swollen hydrocolloid was represented by example 86, at  $6.2 \times 10^6$  dynes/cm<sup>2</sup>. The preferred upper shear modulus limit was represented by example 84 at  $1.5 \times 10^5$  and the most preferred upper shear modulus limit was represented by example 83 at  $41.2 \times 10^3$  dynes/cm<sup>2</sup>.

Examples 87 and 88  
Other Swelling Agents

Examples 87 and 88 demonstrated the use of other non-volatile swelling agents in place of glycerol.

Example 87

To 3.0 parts of crosslinked poly (N-vinyl pyrrolidone) of example 8 was added 7.0 parts propylene glycol and 30.5 parts of distilled water. Once the solution was absorbed by the PNVP, the gel was mixed vigorously with 35.7 parts of the PSA of example 2 (28.0% solids) and 10.7 parts n-heptane until the hydrocolloid appeared evenly dispersed. The coating, drying and laminating follow the procedure for example 65. The resulting gel-adhesive composite was transparent, very adhesive and had a smooth texture. T-peel adhesion to LDPE was 65 gm/cm, which compares favorably with the use of glycerol, as seen in Examples 6-69 and 72-75.

-81-

Example 88

To 3.0 parts of crosslinked poly (N-vinyl pyrrolidone) of Example 8 was added 1.0 parts glycerol, 5 8.6 parts of a 70% sorbitol solution in water and 30.5 parts distilled water. Once the solution was absorbed by the PNVP the gel was mixed vigorously with 35.7 parts of the PSA of Example 2 (28.0% solids) and 10.7 parts n-heptane until the hydrocolloid appeared evenly 10 dispersed. The coating, drying and laminating followed the steps of Example 65. The resulting gel-adhesive composite was transparent, very adhesive and had a smooth texture. T-peel adhesion to LDPE was 66 gm/cm, which compares favorably with the use of glycerol, as seen in Examples 66-69 and 72-75. 15

In accordance with the Patent Statutes, embodiments of the invention have been described. A series of examples have been provided to illustrate the variety of acceptable components according to the scope 20 of the invention. The invention is not to be limited by the description of the embodiments or examples. There are many variations within the scope of the invention. Consequently, for an understanding of the scope of the invention, reference is made to the following claims. 25

30

35

-82-

WHAT IS CLAIMED IS:

1. A composite of a gel dispersed in a pressure sensitive adhesive matrix, comprising:

5 (a) from about 5 weight percent to about 99 weight percent of a pressure sensitive adhesive composition as said matrix;

10 (b) from about 1 weight percent to about 95 weight percent of said gel dispersed in said pressure sensitive adhesive matrix, said gel comprising a hydrocolloid and a non-volatile hydrocolloid swelling agent having a ratio of weight fractions of hydrocolloid to swelling agent of from about 3:1 to about 1:99.

15 2. The composite according to Claim 1, wherein said pressure sensitive adhesive composition is hydrophobic and said hydrocolloid swelling agent is hydrophilic, wherein said gel has a shear modulus of less than about  $6.2 \times 10^6$  dynes/cm<sup>2</sup>, and wherein said gel in said matrix has particle sizes of from about 1 to about 20 600 microns.

25 3. The composite according to Claim 1, wherein said pressure sensitive adhesive composition is an acrylic copolymer comprising:

at least one monomer of an acrylic or methacrylic acid ester of an alkyl alcohol wherein said alkyl alcohol contains from 4 to 10 carbon atoms; and

30 at least one other monomer selected from the group consisting of acrylic acid, methacrylic acid, alkyl acrylates and methacrylates containing 1 to 3 carbon atoms in said alkyl group; acrylamide; methacrylamide; alkyl-substituted acrylamides containing 1 to 4 carbon atoms in said alkyl substituted group; diacetone acrylamide; N-vinyl-2-pyrrolidone; and vinyl 35 perfluoro-n-butyrate;

-83-

wherein said first monomer has a weight percent of from about 85 percent to about 98 percent and said other monomer has a weight percent of from about 2 percent to about 15 percent.

5

4. The composite according to Claim 1, wherein said pressure sensitive adhesive composition comprises at least one polymer selected from the group consisting of polyolefins, and polyvinyl ethers, silicone pressure sensitive adhesives and  
10 polystyrene-polyisoprene-polystyrene block copolymers, a natural or synthetically derived rubber base adhesive composition.

15

5. The composite according to Claim 1, wherein said hydrocolloid comprises a poly (N-vinyl lactam), a polyvinyl alcohol, a polyoxyalkylene, a polyacrylamide, a polyacrylic acid, a polymer having nitrogen in the non-cyclic or cyclic monomeric backbone, a polystyrene sulfonate, a natural or synthetically modified  
20 polysaccharide, an alginate, a xanthan gum, a guar gum, a natural or synthetically modified cellulose, or a linear or crosslinked polyhydroxyalkyl acrylate or methacrylate.

25

6. The composite according to Claim 2, wherein said non-volatile hydrocolloid swelling agent comprises a room temperature liquid polyol, a solid polyol blended with a room temperature liquid polyol, a monoanhydroalditol blended with a room temperature liquid polyol, a monosaccharide, blended with a room temperature liquid polyol, a liquid ether alcohol, or a solid ether alcohol blended with a room temperature liquid polyol.  
30

-84-

7. The composite according to Claim 1, wherein  
said pressure sensitive adhesive comprises  
isooctylacrylate/N-vinyl-2-pyrrolidone copolymer, said  
hydrocolloid comprises poly(N-vinyl pyrrolidone), and  
5 said swelling agent comprises glycerol.

8. The composite according to Claim 1, further  
comprising a broad spectrum antimicrobial agent therein,  
wherein said antimicrobial agent comprises  
10 parachlorometaxylenol, chlorhexidine and its salts,  
iodine, iodophors, poly (N-vinyl pyrrolidone) iodophors,  
silver oxide, silver and its salts, antibiotics or  
combinations thereof.

15 9. The composite according to Claim 1, wherein  
said pressure sensitive adhesive comprises from about 20  
weight percent to about 95 weight percent of the  
composite and wherein said gel comprises from about 80  
weight percent to about 5 weight percent of the  
20 composite, and wherein said hydrocolloid and said  
non-volatile hydrocolloid swelling agent have a ratio of  
weight fractions of from about 1.5:1 to about 1:19.

10. The composite according to Claim 9,  
25 wherein said pressure sensitive adhesive comprises from  
about 25 weight percent to about 90 weight percent of the  
composite, and wherein said gel comprises from about 75  
weight percent to about 10 weight percent of the  
composite, and wherein said hydrocolloid and said  
30 non-volatile hydrocolloid swelling agent have a ratio of  
weight fractions of from about 1:1.5 to about 1:19.

11. An article having a high moisture vapor  
transmission rate, comprising:  
35 a gel-adhesive composite according to Claim 1  
attached to a backing material.

-85-

12. An article according to Claim 11, further comprising a release liner and wherein said backing material comprises a film having moisture vapor transmission properties, a medical drape, a medical dressing, or a medical tape.

13. A method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate, comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel particles;

15 (b) dispersing said gel particles into a hydrophobic solution comprising a pressure sensitive adhesive;

(c) coating said solution on a release liner; and

20 (d) drying said solution to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

14. A method for preparing a composite of gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate, comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent compatible with said hydrocolloid to form swollen hydrocolloid gel particles;

30 (b) dispersing said gel particles into a latex mixture comprising a pressure sensitive adhesive;

(c) coating said latex mixture on a release liner; and

35 (d) drying said latex mixture to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

Fig. 2

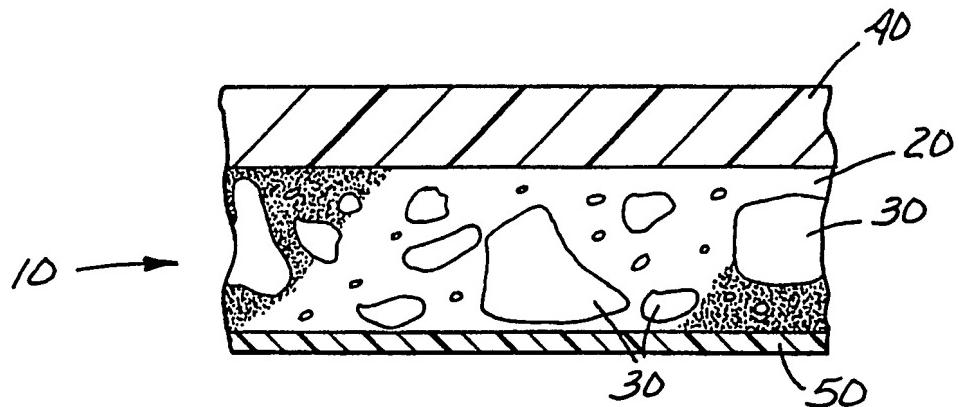
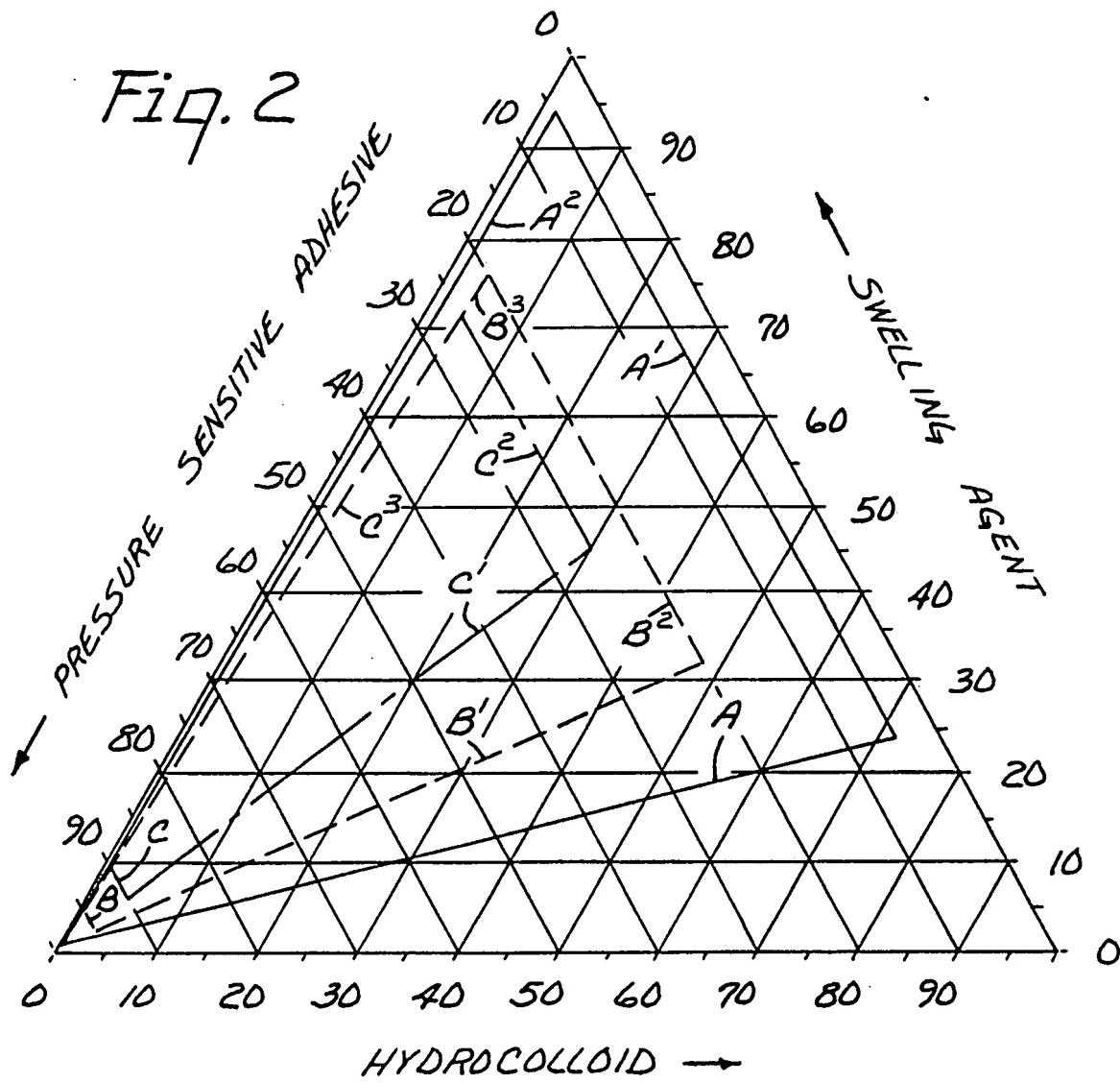


Fig. 1

## INTERNATIONAL SEARCH REPORT

PCT/US 90/07412  
International Application No.

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup>: A 61 L 15/22, 15/58, 15/60, C 09 J 157/00

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC <sup>5</sup>	A 61 L, C 09 J

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	GB, A, 2008000 (KAO SOAP) 31 May 1979 see claims; examples; page 1, line 59 - page 2, line 14; page 2, line 63 - page 3, line 3 --	1-6,9-12
X	EP, A, 0066887 (HOLLISTER) 15 December 1982 see claims; page 4, lines 1-31; page 6, lines 30-31 --	1-6,8-12
X	GB, A, 2046774 (ADVANCE TAPES) 19 November 1980 see claims; examples --	1-14
A	GB, A, 2061732 (KINGSDOWN MEDICAL CONSUL- TANTS) 20 May 1981 --	
A	EP, A, 0072251 (LECTEC CORPORATION) 16 February 1983 -----	

\* Special categories of cited documents:<sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

3rd May 1991

Date of Mailing of this International Search Report

20.06.91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

miss T. MORTENSEN

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9007412  
SA 44071

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/06/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A- 2008000	31-05-79	JP-C-	1010678	29-08-80
		JP-B-	54044688	27-12-79
		JP-A-	54070340	06-06-79
		DE-A-	2848977	17-05-79
		US-A-	4226915	07-10-80
EP-A- 0066887	15-12-82	US-A-	4534767	13-08-85
		US-A-	4578065	25-03-86
GB-A- 2046774	19-11-80	EP-A, B	0017401	15-10-80
		US-A-	4356819	02-11-82
GB-A- 2061732	20-05-81	AU-B-	537462	28-06-84
		AU-A-	6159780	09-04-81
		CA-A-	1151041	02-08-83
		EP-A, B	0026572	08-04-81
		JP-B-	1009864	20-02-89
		JP-C-	1524684	12-10-89
		JP-A-	56045667	25-04-81
		US-A-	4341207	27-07-82
EP-A- 0072251	16-02-83	AU-B-	553343	10-07-86
		AU-A-	7542481	24-03-83
		CA-A-	1206095	17-06-86
		US-A-	4675009	23-06-87